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ACTIVATED CARBON TREATMENT OF UNBLEACHED KRAFT EFFLUENT FOR REUSE

E. W. Lang, et al

Pacific Northwest Environmental Research
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Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse

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A four-year pilot plant program was carried out to investigate the technical and economic feasibility of treating unbleached kraft pulp and paper mill effluent for reuse. Preliminary laboratory studies and cost estimates indicated that the following treatment sequences should be investigated in the pilot plant: 1) primary clarification, carbon adsorption; 2) lime treatment, carbon adsorption; 3) primary clarification, bio-oxidation, carbon adsorption.

Water of reusable quality can be provided from unbleached kraft effluent by several combinations of treatment utilizing activated carbon. Unbleached pulping effluents typically contain about 1000 color units, 250 mg/l TOC, and 250 mg/l BOD. Reusable water quality as defined in this study is 100 color units and 100 mg/l TOC. The most economical treatment is the microlime-carbon process that utilizes low dosages of lime and clarification followed by carbon adsorption in down-flow granular carbon beds. Capital cost for treatment by this process of 9.6 mgd of unbleached kraft effluent from an 800-ton-per-day mill was estimated to be approximately $6.7 millions. Operating costs, inclusive of capital depreciation, were estimated to be $0.30 per 1000 gal and $3.58 per pulp-ton, including credit for the reused water. Carbon adsorption in continuous counter-current stirred contactors was found to have promise of lower operating cost and substantially lower capital costs as compared to adsorption in fixed beds.

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ACTIVATED CARBON TREATMENT OF UNBLEACHED KRAFT EFFLUENT FOR REUSE

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ABSTRACT

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Water of reusable quality can be provided from unbleached kraft effluent by several combinations of treatment utilizing activated carbon. Unbleached pulping effluents typically contain about 1000 color units, 250 mg/1 TOC, and 250 mg/1 BOD. Reusable water quality as defined in this study is 100 color units and 100 mg/1 TOC. The most economical treatment is the microlime-carbon process that utilizes low dosages of lime and clarification followed by carbon adsorption in down-flow granular carbon beds. Capital cost for treatment by this process of 9.6 mgd of unbleached kraft effluent from an 800-ton-per-day mill was estimated to be approximately $6.7 millions. Operating costs, inclusive of capital depreciation, were estimated to be $0.30 per 1000 gal and $3.58 per pulp-ton, including credit for the reused water. Carbon adsorption in continuous counter-current stirred contactors was found to have promise of lower operating cost and substantially lower capital costs as compared to adsorption in fixed beds.

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SECTION I

CONCLUSIONS

1. Unbleached kraft mill effluent can be treated by sequences of lime treatment or primary clarification plus bio-oxidation or primary clarification followed by carbon adsorption in granular carbon columns to provide water suitable for general reuse in the mill.

2. Cost estimates indicate that a microlime-carbon sequence would be the least costly for treating effluent containing 1000 APHA-NCASI color units (CU) and 250 mg/l total organic carbon (TOC) to provide reusable water containing 100 CU and 100 mg/l TOC. For treating 9.6 mgd of effluent from a 800 ton/day mill, the capital cost was estimated to be $6.75 million and the total operating cost inclusive of capital depreciation was estimated to be $0.30 per 1000 gal, or $3.58 per pulp ton, with a credit of $0.06 per 1000 gal for the reused water.

3. Use of lower-cost carbon produced on-site at 10¢/lb vs. a purchased cost of 27¢/lb reduces operating costs of the microlime-carbon sequence by 13%, and capital costs by 8%.

4. Operating costs are reduced about 12% per 1000 gal treated when the pulp production and effluent volume are doubled.

5. Effluent treatment by the microlime-carbon sequence is about 5% lower in capital and 14% lower in operating cost then by the minilime-carbon sequence.

6. Removal of color to 100 CU and of TOC to 100 mg/l by the microlime-carbon sequence requires maintaining a dissolved calcium concentration of about 80 mg/l Ca (minimum of about 40 mg/l) by the use of about 500 mg/l of added CaO, no carbonation, and requires 2.5 lb of activated carbon per 1000 gal effluent treated at a contact time of 1.8 hrs. At these levels, the microlime treatment alone removes 70% of the color, compared to 85-90% at a dosage of about 1000 mg/l CaO in the minilime treatment.

7. The lime-color sludge obtained at 80 mg/l dissolved Ca contains up to 35% solids and filters to a solids content suitable for feeding to a lime kiln.

8. The primary-bio-carbon sequence provides reusable water quality at 10.5 lb activated carbon per 1000 gal of effluent at a contact time

of 3.8 hrs. These requirements caused high capital costs and the resulting total operating costs were \$0.58/kgal or \$10.50/pulp ton, which were about double those for microlime-carbon.

9. The primary-carbon sequence provides reusable water quality at a dosage of 23.4 lb activated carbon per 1000 gal effluent treated and a contact time of 5.3 hrs. These requirements caused high capital and operating costs and made this sequence much more costly than the lime-carbon sequence.

10. Granular carbon rather than powdered activated carbon is the economical choice because high dosage requirements (including the microlime-carbon sequence) necessitate regenerative use of activated carbon even if available at very low cost from mill site production. Regeneration systems for powdered carbon, though under development, have not as yet been applied on a large scale.

11. Fixed-bed carbon adsorption of raw clarified effluent or of water treated by bio-oxidation or lime gave no operating problems. Backwashing of the beds every one or two days prevents buildup of pressure drop.

12. A novel continuous countercurrent process (FACET) for carbon adsorption using stirred tanks of carbon slurries was shown to have considerable promise for reducing capital and operating costs, and its development is being continued.

13. Non-adsorptive mechanisms are responsible for as much as 30% of color removal and 20% of TOC removal, particularly in the primary-carbon sequence.

14. Anaerobic digestion in the equalization basin resulted in substantial increases in non-adsorbable TOC in the form of low molecular weight organic compounds.

15. Interactions between carbon and effluent lead to not-fully-understood color and suspended solids phenomena, particularly in the FACET system.

16. The color of lime treated effluent is subject to increases of approximately 50% upon aging or bio-oxidation.

17. Carbon adsorption removed almost all of the foaming tendency of effluents.

SECTION II

RECOMMENDATIONS

It is recommended that the concept of treatment and reuse rather than discharge be given serious consideration by operating mills and by those planning to install new production and effluent treatment facilities.

This concept appears to be a sound one from an economic standpoint particularly when, as it appears, less severe quality criteria can be applied to treatment for reuse as compared to treatment for discharge, particularly with respect to BOD and TOC. Although a working definition of reusable water quality has been established in this study, i.e. 100 CU and 100 mg/l TOC, and although many internal streams are used today in the kraft mill of even poorer quality, no generally accepted criteria exist and it is recommended that these be established by an industry committee. These criteria necessarily must include additional parameters which were not primary performance criteria in this study. It is also recommended that grants be established to demonstrate reusability of treated effluents on a mill scale, first in selected areas and subsequently on a maximum feasible basis while appropriate operating and product quality parameters are monitored.

It is recommended that Part II of this grant be continued to conclusion to assure availability of low cost carbon from mill sources for application in effluent treatment and reuse.

It is recommended that the development of the FACET carbon adsorption system be continued as a means of reducing the cost associated with activated carbon treatment. In view of the cost per 1000 gal of water treated, it is recommended that application of advanced effluent treatment for color removal be preceded, in order to reduce overall water costs, by a study and/or implementation of suitable and economically advantageous methods of reducing; a) the total effluent load to the treatment system; b) the color that is allowed to enter it; and c) the fluctuations in concentration in the effluent.

Specific questions recommended for further investigation include permissible levels in reused water of dissolved solids such as sodium and calcium salts, heavy metal salts and others; effect of treatment and reuse on temperature levels in critical process areas, effect of dissolved salts on sheet formation, drainage, corrosion, pulp washing, lime mud washing, and scale formation.

SECTION III

INTRODUCTION

St. Regis Paper Company with partial support by EPA has been engaged since July, 1969, in a program for the development of an economical system for maximum water reuse in the kraft pulp and paper industry as a means of water pollution control and water conservation. This program is based on two key concepts: (1) effluent treatment using activated carbon and, (2) on-site production of activated carbon from readily available raw materials, particularly black liquor, with full integration into the kraft mill recovery and power systems to achieve the lowest net cost of activated carbon.

This report covers the work accomplished under Part 1 of the program: effluent treatment using activated carbon. Preliminary results from the laboratory phase (15) and pilot plant (45,46,47) have been reported previously.

Maximum water reuse, though not strictly definable, is assumed to be in the order of 90% reuse. Ten percent of the usual fresh water input to the kraft mill, it is assumed, will be discharged primarily to purge inorganic salts at nonpolluting levels. This effluent would discharge a total organic contaminant load equivalent to 10% or less of present discharges.

Cost estimates made prior to starting this program indicated that treatment of unbleached kraft pulp and paper mill effluent by process combinations involving activated carbon, produced at the mill, and reuse of the treated water would be less costly than treatment by other processes to meet anticipated discharge standards, including standards for color.

The first task of this program was a survey of the literature and a review of information from industry on treatment of effluents and reuse of treated water in pulp and paper mills. The findings of this survey were published in the first report of this program (40). All other activities of Part I are covered by the present report.

The basic possibility of using activated carbon to obtain high-quality effluents, particularly in terms of color removal, was indicated in studies by McGlasson (10,11) and Berger (4).

Treatment of kraft effluents with lime, as reported a number of years ago by Berger (3) and commercially applied by Davis (5), achieves substantial color removal and thus appeared to merit consideration as a treatment step prior to activated carbon. Further reports on commercial installations for lime decolorization of pulp effluents have appeared more recently (7,8,14,18).

The success of biological oxidation systems, particularly aerated lagoons in the southern states, in achieving as much as 90% reduction in BOD-5, and the trend towards more installations of this type, provided sufficient argument to include in this study an investigation of the effectiveness of activated carbon treatment of bio-oxidized kraft effluent.

Thus it appeared that the role of activated carbon treatment might be as the sole treatment step for color and dissolved organics, or as a major second step after lime or biological treatment, or as a polishing step following a combination of lime treatment and biological oxidation.

On the basis of laboratory studies and preliminary cost estimates, given in this report, a decision was made to build and operate a pilot plant at the Pensacola, Florida, St. Regis pulp and paper mill with a capacity of about 30 gpm of unbleached kraft effluent to investigate three sequences of treatment:

Primary clarification, activated carbon adsorption
Lime treatment, carbon adsorption
Primary clarification, biological oxidation, carbon adsorption.

The results from operating this pilot plant from November, 1971, through December, 1972, and cost estimates for treating pulp mill effluents for reuse constitute a major part of this report.

SECTION IV

LABORATORY STUDIES

INTRODUCTION

The purpose of the laboratory study was to help define where and how activated carbon might be used most economically in order to achieve treatment and up to 90% reuse of effluent from kraft pulp and paper mills. Based on laboratory results, and with the aid of preliminary designs and economic estimates as presented in Section V, the available choices were to be narrowed down to three systmes and a pilot plant designed and a pilot plant operation program developed. In this study, two main approaches were pursued in terms of effluents to be treated. These were the treatment of specific effluents for specific reuse, and the treatment of the total effluent for general reuse. It was recognized that the best approach might be a compromise of the two, such as separate treatment of evaporator condensate and turpentine underflow for reuse in lime mud and pulp washing, while combining all other effluents for treatment and general reuse.

For the total effluent, the major treatments studied were primary clarification followed by activated carbon; primary clarification, lime treatment, activated carbon; primary clarification, lime treatment, biological oxidation, and activated carbon; primary clarification, biological oxidation, and activated carbon; and primary clarification, biological oxidation, lime treatment, and activated carbon. In these laboratory studies, "primary clarification" (simulated by filtration) was always carried out separately as a first treatment. Mill scale applications (14,18) and hence design and cost studies (Section XIV) use no clarification ahead of lime treatment. Laboratory treatment methods are described in Appendix B.

These same treatment combinations were studied with the caustic and acid bleach effluents, although general reuse of bleach effluents is considered unlikely until chloride removal can be achieved economically. Only minor reductions can be expected in the chloride content as a result of any of the treatment sequences investigated. Hence, reuse of the bleach effluents in the pulp mill would eventually lead to an undesirable build-up of chloride in the black liquor.

For other specific effluents, the use of activated carbon treatment alone was investigated in this study, although other treatments may also be required. For example, fiber removal from paper machine white water will be necessary before applying activated carbon treatment for the removal of dissolved organics.

By using effluents from the three southern mills of St. Regis, and one other mill with lime treatment, representing a spectrum of modern and older plants, the chances were increased that this program would be of value to the entire pulp and paper industry. The study included laboratory treatment of effluent samples from various mills before any treatment and after full-scale primary, biological, and/or lime treatments. Table 1 summarizes the treatments used in the laboratory study with each of the effluents.

In terms of activated carbon treatment per se, the primary function of the laboratory study was to determine the dosages of carbon required to reach desired concentrations of color and TOC in the various effluents to be tested. These dosage data usually are obtained in the form of adsorption isotherms as described in Appendix B. Carbon dosage data are part of the information required to prepare preliminary designs and make preliminary cost estimates for potential treatment systems. More specifically, for instance, dosage data together with other cost data for the carbon itself as well as for equipment, are major determining factors in deciding between single use of carbon (usually as powdered carbon) and regenerative use of carbon (usually as granular carbon).

Commercially available carbons vary widely in their characteristics and more particularly in their effectiveness in removing dissolved TOC or color from different effluent streams. Although it is an objective of the two-part program to develop an activated carbon for effluent treatment from pulp mill sources (particularly black liquor), this carbon was not available in sufficient quantity for the laboratory program or the subsequent pilot plant operation. By using a wide variety of commercially available activated carbons in the laboratory program, it was possible to select suitable commercial carbons for the pilot plant operation, as well as for potential full-scale applications, and it was also hoped that the information gained would help in the definition of characteristics to be obtained in the carbon made from black liquor. The major part of the laboratory study was devoted to establishing adsorption equilibrium data for carbon as discussed above.

The final selection of the carbon to be used in the pilot plant was made on the basis of additional isotherm work on Pensacola No. 2 Mill effluent (unbleached kraft) and on the basis of comparative adsorption column work. This work was done after reaching the decision (see Section V) to treat unbleached kraft total effluent using granular carbon columns, and it also helped to determine the size of the pilot plant carbon columns.

After selecting the lime-carbon treatment sequence as one of the three pilot plant treatment sequences, (see Section V), additional studies were performed in the area of lime and lime-carbon treatment.

Table 1. LABORATORY TREATMENTS OF EFFLUENTS

Specific effluents	Type of treatment[a]
Turpentine underflow	Carbon
Evaporator condensate	Carbon
Paper machine white water	Carbon
Condensate cooling tower	Carbon
Woodyard	Carbon
Caustic bleach	Carbon and combined[b]
Acid bleach	Carbon and combined[b]
Total mill effluents	
Total mill	Carbon and combined[b]
High solids sewer	Carbon
Low solids sewer	Carbon
Total mill without biological oxidation	Carbon
Total mill with biological oxidation	Carbon
Total mill lime treated	Carbon and bio-oxidation
Simulated pulp mill effluents	
0.05% black liquor solids	Carbon
0.5% black liquor solids	Carbon

[a] All treatments preceded by filtration

[b] Including lime and bio-oxidation in various combinations

Special studies were carried out in two other areas. One of these areas was studies leading to a continuous, countercurrent, fine carbon contacting system called FACET, for which a patent has been awarded (41), and which underwent initial development in the pilot plant. The other area is that of carbon adsorption in an aerated system with or without biological activity.

Significant observations which have some bearing on the selection of a treatment system and its results are discussed in a separate part of this section, including observed color reversion after lime treatment, and adsorption or non-adsorption of compounds in effluents.

SELECTION OF CARBONS FOR EVALUATION

Each of the major manufacturers or suppliers of activated carbons for water treatment was contacted to determine which of their carbons would likely be best for removal of color and TOC from each of the effluents to be studied. Help in selecting carbons for the demonstration was also obtained from a study of the literature and discussions with other investigators working on water treatment. In general, the cost of the carbon and whether it is available in granular or powder form were disregarded. Samples for adsorption studies in powder form were supplied by Westvaco, Calgon, Atlas, Norit, and Barnebey-Cheney.

A list of the carbons used in this study is given in Table 2.

Table 2. CARBONS SELECTED FOR ADSORPTION STUDIES

Westvaco	Calgon	Atlas	Norit	Barnebey-Cheney
AN	F-100	S-51	A	SC
C-190	F-300	KB	F	XZ
WV-L	F-400	DARCO	FQA	
WV-G		XPT	NC	
WV-W		XPS	SG	
WV-M				

RESULTS OF CARBON AND COMBINED TREATMENTS

Evaluation of Activated Carbons

The major means of determining the effectiveness of each type of activated carbon was carbon adsorption isotherms, the procedure for which is described in Appendix B. Six samples of the effluent were treated with six different dosages of powdered carbon, and the results were plotted on log-log graphs of loading of impurity on the carbon *versus* concentration of impurity remaining in the water sample.

Isotherms for four carbons for removal of color from the total mill effluent from mill A are shown in Figure 1. Note that the isotherms all had definite breaks at a color concentration of about 300 CU.

Typical isotherms for removal of TOC are shown in Figure 2. These isotherms employ the same four carbons and the same effluent as the color isotherms above. The TOC isotherms are almost identical for all four carbons and can be represented by a single line.

Such isotherms for color and TOC removal were prepared using two to four commercial carbons for each of the various effluent streams and after pre-treatment by lime or bio-oxidation or both. Over 150 isotherms, not including duplicates and repeats, were prepared.

The reasons for using several carbons for each stream were (1) to indicate which of the commercially available carbons recommended by the manufacturers are best for treating each stream, and (2) to indicate which physical properties, such as pore size, of carbons are best for each stream.

Some of the results of these carbon treatments are less definitive than had been hoped owing to several factors:

- The feed concentration and composition of a given stream often varied considerably over the period of time that samples were taken for the pre-treatment and carbon adsorption experiments.
- Some of the isotherms had very steep slopes owing to high concentrations of poorly adsorbed compounds, such as methanol.
- Some isotherms, particularly for color, were made up of lines of several slopes caused by the several types of components in the water.

Comparisons of Carbons

The most reliable method of comparing carbons for removal of impurities from water samples was to compare the loading of color or TOC per unit weight of carbon at selected concentrations of color and TOC. These loadings were read from the isotherms at color concentrations of 1000, 500, 250 and 100 CU and TOC concentrations of 150, 100 and 50 mg/l, representing intermediate and fairly complete treatment levels.

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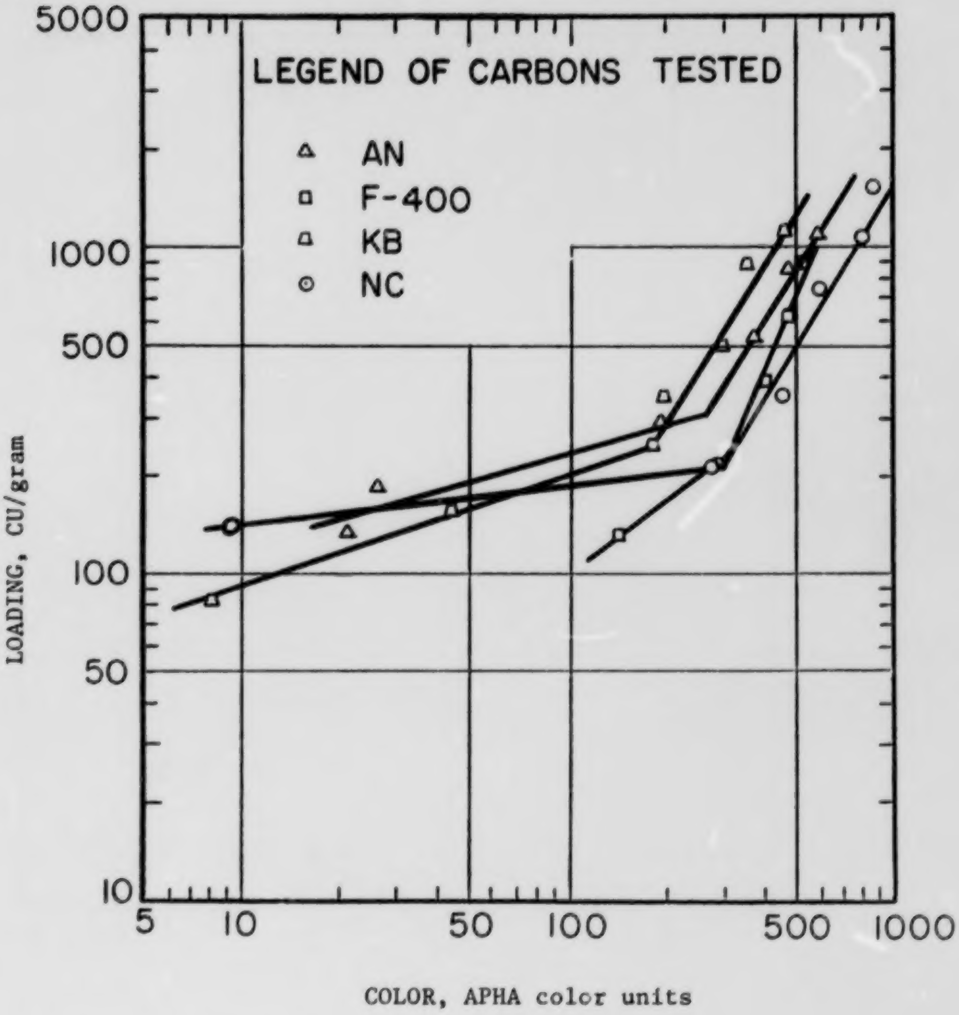


Figure 1. Carbon adsorption isotherms for color removal from total mill effluent

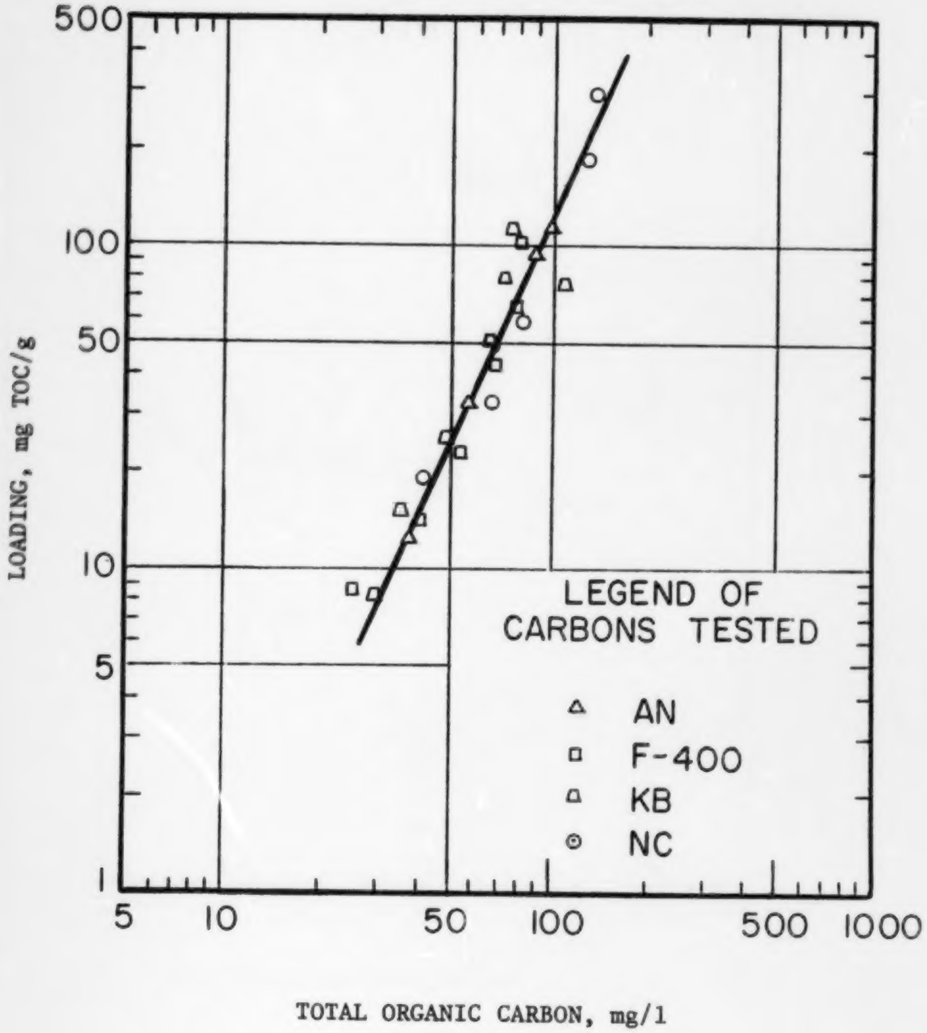


Figure 2. Carbon adsorption isotherms for total organic carbon removal from total mill effluent

Another commonly used method is to compare the concentration of the impurity remaining in the water after equal dosages of the several carbons. Disadvantages of this method are that it requires that all carbons be tested with the same sample of water and that it provides no information on the effects of concentration on loading which isotherms would provide.

In addition to loading capacity, other properties of carbons must be considered in choosing a carbon for a given application. These properties include whether powdered or granular carbon is best, the rates of adsorption, the friability of the (granular) carbon, handling problems, and cost. If a carbon is to be used in a column contactor, it should be evaluated in continuous column tests with the particle size most likely to be used in the future plant scale of operation.

In fully counter-current adsorption, the carbon dosage required to reduce the color or TOC from any feed concentration to some desired level can be calculated by using the following formula:

$$\text{Dosage, g/l} = \frac{Co - D}{Xo} \qquad (1)$$

where:

Co= Initial concentration in CU or mgTOC/l,
D = Desired concentration of color or TOC to be reached
Xo= Loading at Co, CU/g or mgTOC/g.

If a batchwise single - stage treatment is used, the dosage required is:

$$\text{Dosage, g/l} = \frac{Co - D}{Xd} \qquad (2)$$

Where Xd is the loading at the desired final concentration

In practice, the maximum loading reached in a packed column system using granular carbon is about 65% of Xo from the isotherm, resulting in a corresponding increase in the required dosage amounting to about 50% in excess of the dosage calculated using equation (1) above. This difference in loading is due to two major factors. First, a packed column is not a true counter-current contacting system, and only a fraction of the carbon actually is in contact with effluent of the feed concentration, Co, while most of the carbon is in contact with effluent of decreasing concentration in the direction of effluent flow. Second, the equilibrium that is established in a flow system is between the adsorptive surface and the effluent in immediate contact with it, while the bulk effluent remains at a higher concentration. This concentration difference provides the driving force for the transfer of the dissolved substances from the bulk phase through the stagnant water film surrounding each carbon particle and the water in the pores of the carbon. Results taken from a total of 29 isotherms are given in Table 3. These results were obtained using the total mill effluent from two southern kraft mills. The carbons are ranked according to the relative effectiveness of each for removal of color at 500 CU remaining in solution. Note that the ranking would have been different at a lower remaining color concentration, except that the top carbon performed best at either concentration. Note further that top performers in terms of color removal are not the top performers in terms of TOC removal. For Mill B effluent, S-51 and AN carbons were best, while for Mill A the KB and AN carbons were best. For pulp and paper mill effluents, color removal tends to be the more important characteristic of a good carbon. Mill A effluent generally resulted in higher loadings than Mill B effluent, probably because of the presence of sea water in Mill A effluent.

Another comparison of carbons is shown in Table 4. This compares four carbons used to treat paper machine white water from Mill B. Results indicate that the AN and S-51 carbons were superior in color and TOC removal. The C-190 carbon, which showed good color loading, performed poorly on removal of TOC.

Table 3. COMPARISONS OF CARBONS FOR REMOVAL OF COLOR AND TOC FROM TWO MILL EFFLUENTS

Carbon	No. samples averaged	Color removal avg. loading, CU/g at 500 CU	Color removal avg. loading, CU/g at 100 CU	TOC removal avg. loading, mg/l at 100 mg/l	TOC removal avg. loading, mg/l at 50 mg/l
Mill A effluent					
KB	1	1200	200	200	30
AN	4	840	170	110	24
F-400	1	700	125	350	22
NC	1	500	180	250	23
Mill B effluent					
S-51	6	260	140	40	11
AN	8	250	90	30	7
NC	1	250	60	21	8
WV-G	1	145	120	30	-
WV-L	3	140	40	21	8
F-300	1	130	75	100	9
KB	1	110	100	110	30
WV-M	1	60	23	20	1

Similar comparisons of carbons were prepared from isotherms of carbons made with other in-plant and total mill effluents. It was concluded that the most promising carbons for removal of color and TOC from the major mill effluents were AN, S-51, KB, F-300, and NC. Of these five carbons AN, KB, and NC are powdered carbons, and S-51 (as Granular Darco) and F-300 are granular carbons.

Table 4. COMPARISON OF CARBONS FOR REMOVAL OF COLOR AND TOC FROM PAPER MACHINE WHITE WATER FROM MILL B, AT pH 7.7

Carbon	No. samples averaged	Color removal avg. loading, CU/g at 100 CU	TOC removal avg. loading, mg/g at 50 mg/1
AN	3	577	137
S-51	2	279	285
C-190	3	247	65
F-400	2	115	77

Comparison of Treatment Sequences Involving Activated Carbon

The purpose of this program was to determine the best means of treating in-plant and final effluents of pulp and paper mills for water reuse. The most economic method of treating a given stream might be with primary clarification and carbon treatment, or with carbon following lime treatment, primary clarification and bio-oxidation, or combinations of lime treatment and bio-oxidation. The effects of such combinations of pretreatment and adsorption of color and TOC by carbon are illustrated by the results in Tables 5 and 6 for the treatment of a total mill effluent with AN carbon. The treatment methods are described in Appendix B. (All treatment sequences carried out in the lab start with paper filtration, simulating primary clarification.) The carbon treatments are all with 1 g of AN powdered carbon per liter of effluent.

Table 5. EFFECT OF TREATMENT SEQUENCES ON REMOVAL OF COLOR FROM MILL EFFLUENTS

Treatment[a]	Initial color[b] CU	Final color CU	Initial pH
Using total mill effluent from Mill A			
Carbon	948	370	8.6
Bio	833	570	
Carbon	570	180	7.5
Bio	833	570	
Lime	570	45	
Carbon	45	10	7.4
Lime	1380	70	
Carbon	70	8	7.2
Lime	785	64	
Bio	64	185	
Carbon	185	10	7.5
Using total mill effluents from Mills C and D			
Mill C			
No aeration			
Carbon	4590	2500	10.1
Mill C			
With aeration	4590	2025	
Carbon	2025	700	7.5
Mill D			
Lime	-	525[c]	
Carbon	525[c]	90	7.2
Mill D			
Lime	-	525[c]	
Bio (in lab)	525[c]	479	
Carbon	479	190	7.5

[a] Basis of treatments: filtration of the water samples before treatment to simulate primary clarification, single-stage powdered carbon (AN) with dosage of 1 g/l, biological oxidation for 40 hr with nutrients and seed added, lime treatment with dosage of 5 g/l of CaO.

[b] Four different samples of effluent used for five treatment sequences.

[c] The high color levels after lime treatment are not representative of normal mill performance.

Table 6. EFFECTS OF TREATMENT SEQUENCES ON REMOVAL OF TOC FROM MILL EFFLUENTS

Treatment[a]	Initial TOC, mg/l	Final TOC mg/l	Initial pH
Using total mill effluent from Mill A			
Carbon	138	75	8.6
Bio	111	66	
Carbon	66	30	7.5
Bio	111	66	
Lime	66	-	
Carbon	-	-	7.4
Lime	106	67	
Carbon	67	38	7.2
Lime	106	67	
Bio	67	46	
Carbon	46	23	7.2
Using Mill C effluent: before and after aeration basin			
No aeration			
Carbon	713	570	10.1
With aeration	713	183	
Carbon	183	90	7.5

[a] Basis of treatments: filtration of the water samples before treatment to simulate primary clarification, single-stage powdered carbon (AN) with dosage of 1 g/l, biological oxidation for 40 hr with nutrients and seed added, lime treatment with dosage of 5 g/l CaO.

When only carbon was used, the color was reduced from 948 to 370 CU with a dosage of 1 g/l (see Table 5). When this effluent sample was first treated by bio-oxidation, the color was reduced only slightly (to 570 CU). The subsequent carbon treatment reduced the color to 180 CU with a dosage of 1 g/l. When lime treatment was used following bio-oxidation the color was reduced sharply to 45 CU, and a dosage of 1 g/l of carbon reduced it further to 10 CU. The use of bio-oxidation following lime treatment was not as effective as the reverse treatment, since the color increased during the bio-oxidation. (This reversion of color after lime treatment is discussed later in this section.) This increased color was readily removed to a level of 100 CU with a carbon dosage of 0.1 g/l and to 10 CU with a dosage of 1.0 g/l.

The effects of the same treatment sequences on TOC removal from the same total mill effluent are given in Table 6. With carbon alone, the TOC was reduced from 138 mg/l to 75 mg/l with a single dosage of 1 g/l. Bio-oxidation reduced the TOC from 111 to 66 mg/l, and carbon treatment further reduced it to 30 mg/l with a dosage of 1 g/l.

Tables 5 and 6 also compare treatment methods on the basis of color and TOC removals using effluents from Mill C before and after bio-oxidation at the mill. Carbon treatment of the effluent before bio-oxidation with a dosage of 1 g/l reduced the color from 4590 to 2500 CU and reduced the color after bio-oxidation from 2025 to 700. After lime treatment at Mill D, carbon treatment with a dosage of 1 g/l reduced the color of the mill effluent to 90 CU. Bio-oxidation of this lime-treated effluent reduced the color only slightly, and carbon was less effective for color removal than before the effluent was bio-oxidized. The data in Table 6 for treatment of samples from Mill C show that the aeration basin reduced the TOC from 713 to 183 mg/l and that treatment at 1 g/l further reduced the TOC to 90 mg/l.

The tentative conclusions drawn from this comparison of treatment sequences on total mill effluent, when the goal is reduction to less than 100 CU and less than 50 mg/l TOC, are that primary emphasis in the subsequent studies should be placed on carbon treatment, on bio-oxidation followed by carbon treatment, on lime treatment, and on lime treatment followed by carbon treatment. It appears that treatment sequences including both bio-oxidation and lime treatment before carbon treatment offer comparatively less promise for economical treatments of mill effluents for reuse. These conclusions are based on activated carbon being produced at low cost from black liquor at the mill site, which is the original basis of this program. Goals of different color or TOC levels for the treated water will affect the comparisons of treatment sequences, as will changes in the relative feed levels of color and TOC. It should be noted that in the comparison presented, the controlling impurity is color.

FINAL SELECTION OF COMMERCIAL CARBON FOR PILOT PLANT

As will be discussed in Section V, the selection from the many alternatives was narrowed to further work on three treatment sequences using total mill effluent (unbleached) and using a granular rather than powdered carbon adsorption system.

A review of available information, such as is presented in Table 3, on treating Mill B effluent (Pensacola No. 2 Mill, chosen as the pilot plant site), indicated that Atlas S-51, Westvaco AN, Atlas KB, and Calgon F-300 gave the best overall results. Of the carbons available in granular form, the ranking of the carbons is (1) Atlas Granular Darco, (2) Calgon F-300, and (3) Westvaco WV-L. Similar comparisons were made of the candidate carbons using additional samples of Pensacola No. 2 Mill effluent, in-plant streams, and synthetic effluent prepared by diluting spent pulping liquor to the concentration equivalent to that of mill effluents (containing 0.05% black liquor solids).

The conclusion from these isotherm evaluations was that the most promising carbons were Atlas Granular Darco and Westvaco granular carbons. The rates of adsorption of these carbons were compared in a series of dynamic column adsorption runs using Pensacola No. 2 Mill effluent at a superficial flow velocity of 1 to 2 gpm/ft^2 in 2-in. columns containing equal weights of carbon (about 4-ft beds). The carbons included Atlas Darco 20 x 40 and 8 x 30 and Westvaco WV-L 8 x 30, WV-W 20 x 50, WV-M 20 x 40. In these tests, the two Darco carbons were superior to the Westvaco carbons of corresponding size in the rate and degree of removal of color and TOC. These column adsorption runs showed that the removal of color from the mill effluent would be more difficult than the removal of TOC in reaching the selected goals of 100 CU and 50 mg/l TOC. Therefore the properties of loadings and rates of removal of color were of prime importance in judging which carbon should be used in the pilot plant.

Results of one of the side by side comparisons are shown in Figure 3, comparing cumulative loadings of color and TOC on granular Darco and WV-M carbons.

The low rates of removal of color in both column tests indicated that the contact time of water in the pilot plant or commercial columns would be much longer than is commonly used in carbon treatment of municipal wastewater. To provide the longer time, it was decided to use a low flow rate of 1 to 2 gpm/ft^2 of cross sectional area of the columns. At this low flow rate, pressure drop would be low and pumping cost would not be an important factor in operating costs in a commercial unit. Therefore, it was decided that to gain as much external area of carbon as possible while still maintaining a reasonable pressure drop, 20 x 40 mesh carbon should be used. The 20 x 40 mesh carbon has an external surface area about four times that of the more generally used 8 x 30 mesh carbon and thus gives a

Column A	Column B
Darco 20 x 40	Westvaco WV-M 20 x 40
1000g, 2.381 liters	1000g, 1.981 liters
1.01 gpm/ft^2	1.01 gpm/ft^2
2.1 bed vols./hr	2.6 bed vols./hr

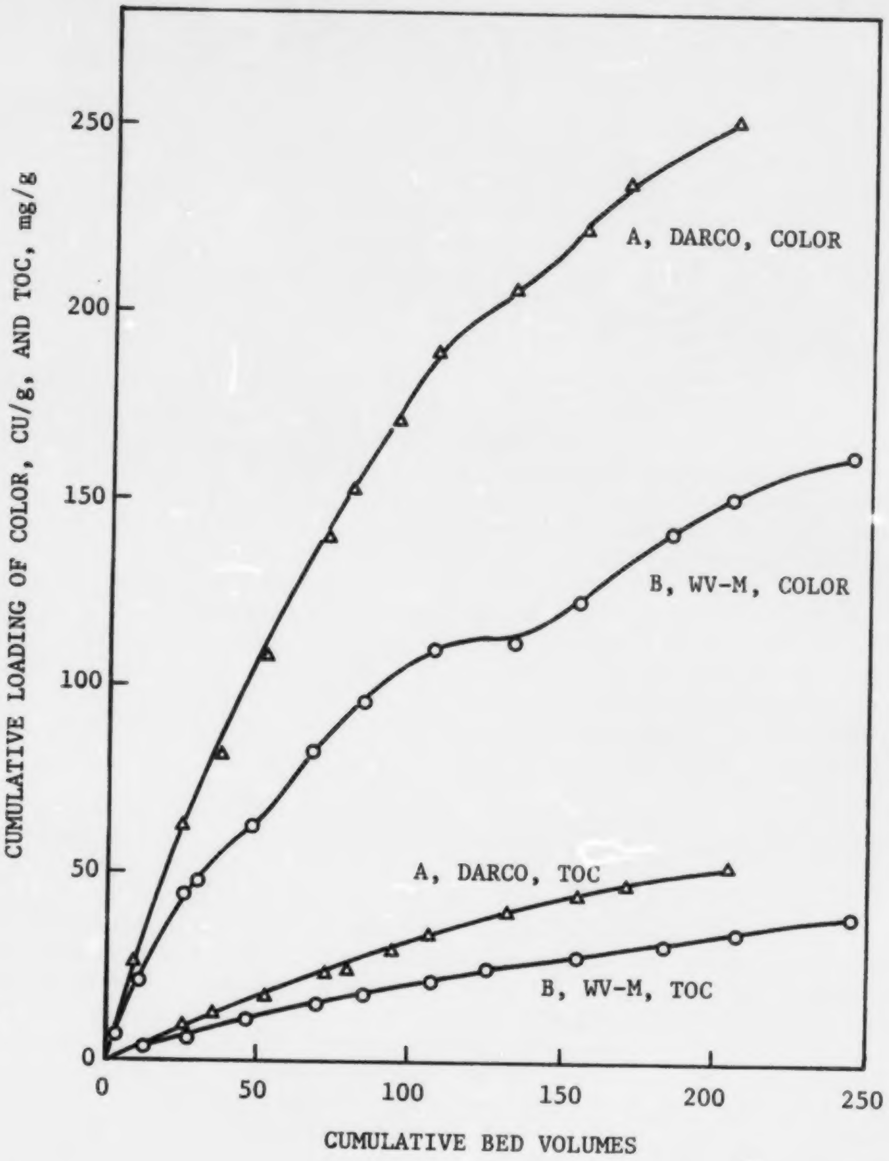


Figure 3. Comparison of cumulative loadings on Darco and WV-M carbons in simultaneous 2-inch column tests

much higher rate of adsorption. A finer size of Granular Darco (Darco XPT) was available which had a particle size range (40 x 140 mesh) that was close to the 60 x 140 size considered desirable for the FACET system as described in Sections V and VI. Therefore, Darco XPT was also evaluated in isotherm and column tests and found to be very similar to Darco 20 x 40 in equilibrium adsorption properties and the rates of removal were about twice those with Darco 20 x 40.

Both the Darco 20 x 40 and the 40 x 140 carbons were evaluated for resistance to attrition in stirring tests and by pumping the Darco XPT as a slurry. The resistance of the Darco carbons to attrition was not as high as some carbons but was considered satisfactory.

Atlas Granular Darco was finally selected for use in the pilot plant on the basis of the following points:

- It had generally superior adsorption capacities and rates of adsorption for color and TOC.
- The Atlas carbon was available in the two size ranges needed for the pilot plant.
- The raw material for the Atlas carbon (lignite) is similar to the lignin-derived raw material to be used in producing activated carbon from kraft pulping liquor under Part II of the EPA - St. Regis program.
- The Atlas carbons were lower in price - $0.25/lb. for the 20 x 40 mesh carbon and $0.17/lb for 40 x 140 mesh carbon than the other candidate granular carbons, which sold at about $0.29/lb.
- Attrition loss of the Atlas 40 x 140, which is an important consideration for the FACET carbon, was only slightly greater than that of other granular carbons.

ADDITIONAL STUDIES

Lime and Lime-Carbon Treatment

After the selection of the lime-carbon treatment sequence of total mill effluent as one of the sequences to be piloted (see Section V), further experimental work was done to determine more closely the effect of different combinations of lime and carbon dosage on the resultant color and TOC levels. As described in Appendix B, a dosage of 5000 mg/l CaO was used in earlier laboratory studies, as compared to the dosage of 1000-2000 mg/l CaO that was later found to be satisfactory in plant tests at Interstate Paper Co. at Riceboro, Ga. and Continental Can Corp. at Hodge, La., (14,18).

Table 7 shows results obtained at different lime dosages in one particular effluent sample (Pensacola No. 2 Mill effluent). Table 8 shows the effect of different combinations of dosages of lime and carbon, where the sample was only filtered after lime treatment and before carbon treatment, i.e. no carbonation was used to remove soluble lime.

Table 7. LIME TREATMENT OF UNBLEACHED KRAFT EFFLUENT

CaO dosage, mg/l	Color, CU	TOC, mg/l
Raw	1585	245
200	1375	204
400	584	181
800	277	146
1200	257	136

Table 8. LIME-CARBON TREATMENT OF UNBLEACHED KRAFT EFFLUENT

Dosage, mg/l		Color, CU	TOC, mg/l	CaO mg/l[b]	pH
CaO	Carbon[a]				
0	0	1675	234	-	10.7
0	5000	413	90	-	10.1
200	1000	438	105	14	11.8
200	5000	177	78	14	11.8
400	1000	61	76	154	12.3
400	5000	6	67	98	12.2
800	1000	56	72	539	12.4
800	5000	8	62	504	12.4
1200	1000	21	70	832	12.7
1200	5000	1	62	714	12.7

[a] Darco S-51

[b] Concentration found in filtered treated effluent

Results in Table 7 indicate that 63% of the color was removed at a dosage of 400 mg/l CaO, and that removal in this case leveled off at about 82%. Table 8 shows, at very similar initial concentrations, that 1 g/l activated carbon is sufficient to reduce the color below 100 CU if 400 mg/l CaO had been used. Higher lime dosages were unnecessary in conjunction with 1 g/l carbon, while higher carbon dosages were unnecessary after 400 mg/l CaO or higher, and insufficient at lower lime dosages. Table 7 indicates that higher lime dosages alone were also unable to reduce the color below 100 CU in this effluent. These results indicated generally that an optimum combination lime and carbon treatment might be developed in the pilot plant requiring substantially lower lime dosages than are employed if only lime is used for color removal.

Color Changes of Raw and Treated Effluents

In the course of laboratory work on the lime-bio treatment sequence, color increases were observed when lime treated effluent was bio-oxidized. The first two lines in Table 9 summarize these results. It was believed that these increases were rather significant, particularly since color increases were also observed at that time in the natural aeration bio-oxidation ponds of the Riceboro, Ga., mill of Interstate Paper Co. (18), and later at Continental Can Corp. at Hodge, La., (14) where lime treatments before bio-oxidation are being operated on a commercial scale.

Subsequent laboratory work shown in lines 3-7 of Table 9 indicated that color of lime treated effluent usually increases upon aging by about 50%, with the exception of one out of 6 samples which showed a 28% decrease.

At the same time it was observed that carbon treated effluent tends to decrease in color, while raw effluent exhibits some instability, showing a decrease first and then an increase.

Table 9 (last line) also shows results observed during pilot plant bio-oxidation of unbleached effluent for comparison, indicating a 15% color reduction during bio-oxidation.

These results indicate a lower degree of stability of color than expected, particularly since the color of kraft mill effluent is generally held to be non-degradable in the usual aerated lagoon treatment system. Particularly in the case of lime treatment, treatment results should be assessed giving full consideration to potential color increases during subsequent bio-oxidation or storage.

Table 9. COLOR CHANGE OF KRAFT EFFLUENT

Effluent	No. of Samples	Initial color, CU			Final color, CU		Aging time, days	Sample size, gal.	Sample pH	
		lime tr.	carbon tr.	raw	bio-oxid.	aged			initial	final
Caustic bleach	2	67	-	-	130	-	-	-	7.0	-
Unbl. total mill	3	46	-	-	104	-	-	-	7.0	-
Unbl. total mill	2	166	-	-	-	242	0.21	40	7.0	-
Unbl. total mill	1	68	-	-	-	100	6	40	7.0	-
Unbl. total mill	1	184	-	-	-	133	5	40	7.0	-
Unbl. total mill	1	184	-	-	-	313	4	0.26	7.0	9.0
Unbl. total mill	1	184	-	-	-	268	4	0.26[a]	7.0	8.8
Unbl. total mill	1	-	119	-	-	60	20	0.26	-	-
Unbl. total mill	1	-	-	1180	-	1136 1305	4 11	400 400[b]	10.1 -	8.2 -
Unbl. total mill[c]				950	810	-	-	-	10.2	8.6

[a] kept dark

[b] same sample as 4 day, 400 gal sample

[c] pilot plant bio-oxidation

Adsorption of Specific Compounds

Each of the effluents studied contains a mixture of organic chemcial compounds. Usually, a few or none of these compounds are identified in effluent treatment work beyond being reported as BOD, color, COD, or, in this study, primarily as color and TOC. The adsorption of organic substances from mixed solution is a complex phenomenon, possibly owing to the effect of one substance on the adsorption of another. This can manifest itself in preferential adsorption of one substance over others, non-adsorption if a substance is only weakly adsorbed at best, or the displacement of a weakly adsorbed by a strongly adsorbed substance. This selective or preferential adsorption must be kept in mind in the evaluation of equilibrium adsorption data.

Concentrations of some specific compounds have been determined in a number of tests in this study for two reasons. One is that, from a commercial applications standpoint, this information may indicate opportunities for recovery of by-products by adsorption - desorption cycles with activated carbon. The return from the scale of such by-products could be credited against effluent treatment costs. The turpentine decanter underflow, which was studied in the laboratory for removal of specific compounds, may be promising in this respect due to its content of turpentine fractions and other organics. Figure 4 presents the adsorption isotherm of loading vs. concentration for carbon treatment of turpentine underflow. Also given is an adjusted isotherm with methanol subtracted from the TOC content, an isotherm for acetone, and an isotherm for dimethyl sulfide plus dimethyl disulfide. These compounds were identified by using gas-liquid chromatography. In this experiment, methanol was found not to be adsorbed and about 20% of TOC was not identified. The initial conclusion based on overall TOC adsorption in this example would have been that this carbon is ineffective. However, isotherms for specific compounds and the methanol-free TOC would suggest that this carbon is reasonably efficient for removing components other than methanol, thus potentially yielding a deodorized water containing some methanol that could be reused in the mill. This phenomenon has meanwhile been further explored in a separate study and a patent application has been filed.

Adsorption Rates

During the course of the laboratory studies, a limited amount of time was devoted to an examination of the factors affecting adsorption rates, i.e. the rate at which impurities defined as TOC or color are removed from effluent by activated carbon.

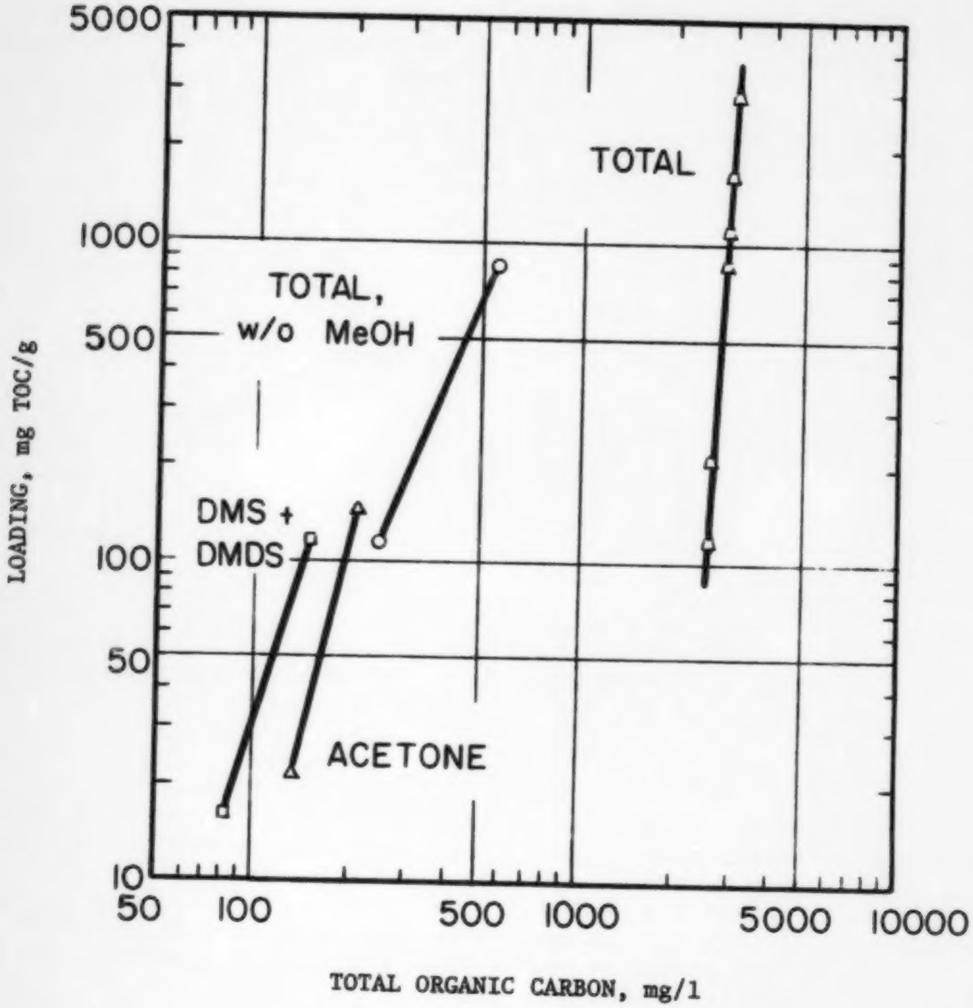


Figure 4. Carbon adsorption isotherms for specific compounds in turpentine underflow

A major factor affecting adsorption rate is particle size. If one assumes that the equilibrium loading is not affected by particle size, then the smaller particles should adsorb at a higher rate because the distance a solute must travel within the porous structure of the carbon is decreased. Weber concluded (15) that rate is proportional to the inverse of the diameter squared, or $1/d^2$. However, in another study, Weber reports for 50% ABS removal from solution by two different sizes (350 and 670 micron) that rates increased proportional to $1/d^{2.9}$. Melter (11) reports rate proportional to $1/d^2$, while Berger (10) found on pulping effluents that rates were proportional to $1/d^{0.5}$.

In this laboratory study, rates were evaluated in stirred batch tests where carbons of four different particle size ranges were added to unbleached kraft total mill effluent from Mill A at dosages of 1, 5 and 10 g/l. Results indicate a proportionality of TOC adsorption rates to the inverse of diameter to some power, with the power varying between 1.6 and 3.0 depending on the degree of loading at which rates were evaluated, i.e. power of 1.6 at 20%, 2.0 at 30% and 3.0 at 50% of loading. In other words, the more the carbon is loaded the more of a disadvantage the larger particle size presents compared to the smaller size. However, this information was not later borne out fully by the comparison of rates in the adsorption columns and the FACET systems in the pilot plant. In these pilot plant runs the rate vs particle size relationship or TOC removal appeared to be closer to proportionality to $1/d^2$ at loadings normally above 50% of isotherm equilibrium loadings, and perhaps even closer to $1/d^{1.6}$ if rates had been compared at strictly equal loading on the carbon.

The effect of dosage on rate would be expected to cancel out if rate is expressed as mgTOC/g carbon x hr. However, rates at higher dosages were actually found to be lower.

SECTION V

SELECTION OF EFFLUENT TREATMENT SYSTEMS TO BE EVALUATED IN THE PILOT PLANT

INTRODUCTION

A laboratory program (see Section IV) was carried out to determine the properties of various streams in three St. Regis kraft pulp and paper mills and to provide a basis for selecting which streams have the greatest promise for reuse when treated. Treatments of the various in-plant and final effluent streams were evaluated in the laboratory. These treatments included bio-oxidation, lime treatment, and activated carbon adsorption. Combinations of these treatments were also evaluated to permit selection of treatment sequences to be used in the pilot plant.

As a further input to selection of treatment sequences for the pilot plant, order-of-magnitude cost estimates were made for treatment of effluents from two St. Regis pulp and paper mills with the candidate treatment sequences. The selection of effluents to be treated and of effluent treatment sequences, as well as the result of the cost estimates, are presented in this section.

These estimates were based on total mill effluents from kraft pulp mills not having bleaching operations because the chloride of the bleach water would not be removed in the treatments and would make it unsuitable for reuse as general mill feed water. The cost estimates included the following combinations of primary clarification (primary), lime treatment (lime), primary clarification combined with lime treatment (primary/lime), (as carried out on a mill scale (14,18)), biological oxidation (bio), and carbon adsorption (carbon):

primary, bio
primary, bio, carbon
primary, carbon
primary, lime
primary, lime, carbon
primary/lime, carbon

The carbon treatments included use of powdered carbon without regeneration of the carbon, granular carbon with regeneration, and a new counter-current continuous process called FACET in which an intermediate size carbon is used.

These estimates indicated that the use of powdered carbon was not practical nor economical and that both column adsorption using granular carbon and slurry contacting using the FACET process should be investigated in the pilot plant. The treatment sequences selected for study in the pilot plant to give reusable quality water were:

primary/lime, carbon
primary, bio, carbon
primary, carbon

(The actual execution of the primary/lime, carbon sequence in the pilot plant used a holding pond to smooth out concentration variations and inadvertently acted as a primary clarifier before lime treatment.)

In each sequence both granular carbon column and FACET slurry carbon processes would be used. The cost estimates indicated that the total fixed and direct operating costs for these sequences would range from \$0.16 to \$0.29 per kgal in commercial installations.

In view of the demonstrated success and reliability of carbon column adsorption process for treatment of municipal wastewater, compared with the unproven status of the FACET process, it was decided that the major emphasis in the pilot plant would be on the carbon column process.

SELECTION OF EFFLUENTS TO BE TREATED

Selection Procedure

The selection procedure consisted of eliminating the less desirable effluent systems on the basis of quantitative comparison and judgement against different criteria which were derived from the project objectives. The effluent systems considered in this study are listed below, including a brief argument for the acceptance or rejection of each.

Total Mill Effluent Without Bleach Effluent

One of the effluent systems considered was the treatment of total mill effluent exclusive of bleach plant effluent, by carbon or by carbon following bio-oxidation and/or lime treatment. This was the approach selected for the pilot plant.

Production of a general mill feed water from an unbleached kraft total mill effluent appeared to be technically feasible. This was indicated by laboratory results of this program and by results reported by others. Activated carbon plays an important role in various treatment sequences capable of producing reusable water.

Economically, the production of reusable water appeared to be competitive when compared with treatment and disposal at anticipated more-stringent near-future disposal standards.

Total Mill Effluent Including Bleach Effluent

Treatment of total mill effluent, including bleach plant effluents, by carbon or by carbon sequentially combined with bio-oxidation and/or lime treatment had also been considered and had been rejected. The inclusion of bleach plant effluents (from chlorine-based bleach systems) in the total mill effluent was considered undesirable because the chloride ion would build up in the recycled water. Laboratory investigations showed that the chlorine content of bleach effluents is essentially not reduced by activated carbon, or by any of the treatment sequences considered in this program. If a chloride removal process such as ion exchange or reverse osmosis were to be considered at a later time, separate treatment of bleach plant effluent would probably be the approach to take. Chloride removal could then follow lime or lime plus activated carbon treatment of bleach plant effluent.

In-Plant Effluents

Treatment of in-plant effluents by activated carbon in a separate unit for each effluent had been considered as the major alternative to total mill effluent treatment. It had been found that a substantial part of the reuse of in-plant effluents that can ultimately be achieved does not, or not yet, require activated carbon treatment. Moreover, the favorable cost estimated for the total mill effluent treatment approach, and the lesser complexity of that approach in terms of actual operation and of its development, argued against pursuing treatment of individual effluents under this program.

PRELIMINARY SELECTION OF TREATMENT SEQUENCES AND CARBON ADSORPTION SYSTEMS

Selection Procedure

The preliminary selection of treatment sequences to be studied in the pilot plant proceeded along the following steps:

(1) Identification of potential sequences.
(2) Determination of reusable water quality requirements.
(3) Laboratory evaluation of the potential sequences with effluents from the three southern mills of St. Regis and from one other mill which uses lime treatment of the total mill effluent.

(4) Preliminary selection of sequences based on laboratory results and judgement of comparative economics.
(5) Consideration of variants within these sequences, particularly with regard to the carbon adsorption step.

Identification of Potential Treatment Sequences

The following treatment sequences were considered to have sufficient merit to warrant study in the laboratory:

(1) Primary clarification followed by activated carbon adsorption;
(2) Primary clarification, lime precipitation, activated carbon adsorption;
(3) Primary clarification, biological oxidation, activated carbon adsorption;
(4) Primary clarification, lime precipitation, biological oxidation, activated carbon adsorption;
(5) Primary clarification, biological oxidation, lime precipitation, activated carbon adsorption.

Determination of Reusable Water Quality Requirements

Water quality requirements are usually expressed in terms of a numerical maximum or range of a number of properties such as color, dissolved solids, etc. Table 10 presents such numerical values based on several references. Although the TAPPI values are used as guidelines for new mills, their basis is a survey of industry practice dating back to 1948, rather than a specific determination of requirements. A TAPPI committee was set up at the 1970 TAPPI Air and Water Conference for the determination of actual water quality requirements at various points of use in the kraft process. The absence of BOD specifications in the TAPPI standards in Table 10 is noteworthy.

Table 10. RANGES OF DESIRED PROPERTIES OF PROCESS WATER FOR UNBLEACHED KRAFT MANUFACTURE

Property	St. Regis proposal 5/1/69[a]	TAPPI E601 S-53[b]	TAPPI E603 S-49[c]
Turbidity, mg/l	5-25	100	25
Color, CU	10-80	100	5
pH	6.5-8.0	-	-
Total alkalinity, mg/l	20-150	150	75
Hardness, mg/l $CaCO_3$	5-200	200	100
Dissolved solids, mg/l	50-500	500	250
Chloride, mg/l	10-150	200	75
Fe, mg/l	0.5	1	0.1
Mn, mg/l	0.3	0.5	0.05
COD, mg/l	0-12	-	-
BOD, mg/l	0-5	-	-

[a] Based on NCASI Bulletin 203 (48)

[b] Specification for chemical composition of process water for kraft paper manufacture; tentative standard, corrected August, 1953.

[c] Specification for chemical composition of process water for manufacture of soda and sulfate pulps; tentative standard, December, 1949.

Early in this program an effort was made within St. Regis to collect water quality standards for the various points in the process of making pulp and paper. The results of this effort, compiled in table form with accompanying comments, are included in this report as Appendix A.

As a result of this effort, it was realized that the tentative TAPPI standards in Table 10 may well be over-specifying some of the water quality requirements of an unbleached kraft mill, except boiler feed water which requires further treatment. Water of 100 CU and 50 mg/l TOC (total organic carbon), equivalent to about 25-100 mg/l BOD, was tentatively considered to be adequate as a general mill feed water (later changed to 100 CU and 100 mg/l TOC). It was considered possible that problems such as slime growth might arise at some of the water use points due to specific organic compounds or due to the general BOD. However, such problems as might arise will most probably have an economical remedy, such as the addition of slimicides or a downward adjustment of the TOC specification for part of the mill feed water. Thus, the tentative targets of 100 CU and 50 mg/l TOC were considered a reasonable basis to proceed on.

Other water properties were not considered in the selection of treatment sequences, although their ultimate importance is recognized. Consideration of color and TOC was believed to be sufficient, since removal of TOC and color is the main purpose of the treatment systems under development. Differences in efficiency and cost between the various systems are expected in this area and are of prime importance. Consideration of possible differences in removal of dissolved inorganics or in recycle water temperature was deferred.

Laboratory Evaluation and Preliminary Selection of Treatment Sequences

The laboratory evaluation of the above identified treatment sequences has been discussed in Section IV and has also been reported (15).

Table 11 and 12 repeat the data on color and TOC removal presented in Tables 5 and 6 and additionally present data on dosages for two- and three-stage treatment with powdered carbon estimated from isotherm data by the procedure described in Appendix B.

Carbon treatment alone is seen to be capable of achieving the tentative standards of 100 CU and 50 mg/l TOC. The carbon dosages for both color and TOC removal are about equal when treating Mill A effluent. For Mill C effluent, substantially higher carbon dosages are required with TOC being the dosage determining factor.

The use of lime or bio pretreatments results in substantial reductions in the carbon dosage in all cases. The bio treatment is, as expected, more effective for removing TOC than for removing color; therefore, color removal becomes the dosage determining factor after bio treatment (unless a partial bio treatment is used). Lime pretreatment, in contrast, is more effective for color removal. Thus, TOC removal after lime treatment becomes the dosage determining factor. (Caution is indicated, however, by color increases observed in laboratory biological oxidations following lime treatment, as discussed in Section IV.)

When comparing the carbon dosages required to reach 100 CU and 50 mg/l TOC in a three-step treatment (lime-bio-carbon and bio-lime-carbon) with dosages required in the two-step lime-carbon treatment, it appears that their is little or no carbon dosage advantage in the three-step treatments. Since volumetric flow through a treatment system is a major cost determinant, a third treatment step cannot be justified on the basis of

Table 11. EFFECT OF TREATMENT SEQUENCES ON REMOVAL OF COLOR FROM TOTAL MILL EFFLUENTS

Treatment[a]	Initial color,CU[b]	Final color,CU	Initial pH	Treatment with carbon[c]: with 1g/1 carbon: color,CU	with 1g/1 carbon: % Removal	with 1g/1 carbon: Loading CU/g	dosage to 100 CU,g/1: 1 stage	dosage to 100 CU,g/1: 2 stages	dosage to 100 CU,g/1: 3 stages
Mill A									
Carbon	948	-	8.6	370	61	580	3.4	0.91	0.58
Bio	833	570							
Carbon	570	-	7.5	180	68	390	1.6	0.61	0.48
Bio	833	570							
Lime	570	45							
Carbon	45	-	7.4	10	78	35	d	-	-
Lime	1,380	70							
Carbon	70	-	7.2	8	87	62	d	-	-
Lime	785	64							
Bio	64	185							
Carbon	185	-	7.5	10	95	175	0.10	-	-
Mill C									
Carbon	4,590	-	10.1	2,500	46	2,100	17.3	2.3	1.10
Bio (at mill)	4,590	2,025							
Carbon	2,025	-	7.5	700	66	1,300	8.4	1.77	1.02
Mill C									
Lime (at mill)		525[e]							
Carbon	525[e]	-	7.2	90	83	430	0.80	0.30	0.24
Lime (at mill)	-	525[e]							
Bio	525[e]	479							
Carbon	479	-	7.5	190	60	290	5.30[f]	1.30	0.74

[a] All samples of water were filtered before treatment to remove suspended solids (simulating primary clarification).

[b] Four different samples of effluent were used for five treatment sequences.

[c] Westvaco Aqua Nuchar.

[d] No carbon needed to reach 100 CU.

[e] High color not considered representative of normal mill performance.

[f] Poor adsorption indicated by steep isotherm.

Table 12. EFFECTS OF TREATMENT SEQUENCES ON REMOVAL OF TOC FROM TOTAL MILL EFFLUENTS

				Treatment with carbon[b]					
				with 1g/1 carbon			dosage to 50/mg/1 TOC,g/1		
Treatment[a]	Initial TOC, mg/1	Final TOC, mg/1	Initial pH	TOC, mg/1	% Removal	Loading, mg/TOC/g	1 stage	2 stages	3 stages
Mill A									
Carbon	138	-	8.6	75	44	53	2.70	0.86	0.57
Bio	111	66							
Carbon	66	-	7.5	30	55	36	0.20	-	-
Bio	111	66							
Lime	66	-							
Carbon	-	-	7.4	23	-	-	-	-	-
Lime	106	67							
Carbon	67	-	7.2	38	43	30	0.19	-	-
Lime	106	67							
Bio	67	46							
Carbon	46	-	7.2	23	50	23	-	-	-
Mill C									
Carbon	713	-	10.1	570	20	140	29.0	5.20	3.20
Bio (at mill)	713	183							
Carbon	183	-	7.5	90	51	90	4.40	1.20	0.73

[a] All samples of water were filtered before treatment to remove suspended solids (simulating primary clarification).

[b] Westvaco Aqua Nuchar.

marginal contaminant load reductions for the remaining two steps. This comparison of treatment sequences for total mill effluent, when the goal is reduction to less than 100 CU and less than 50 mg/l TOC, serves to eliminate the three-step sequences from further consideration.

Goals of different color or TOC levels in the treated water will affect the comparison of treatment sequences. Changes in the concentration of color and TOC in the water being treated will also affect the economic comparison. Because of the variability of effluents from mill to mill, the effect of color and TOC of the feed water on capital and operating costs must be included in the economic comparison of treatment sequences.

Variants in Carbon Treatment Systems

The conventional choice to be made for carbon treatment is between (a) a granular carbon system including adsorption and carbon regeneration; or (b) a powdered carbon system including adsorption and carbon disposal after single use.

A granular carbon adsorption system conventionally uses the carbon in packed columns, the liquid being purified while flowing through the bed of carbon. In a powdered carbon system, the carbon is contacted with the liquid in agitated tanks, followed by clarifiers to remove the carbon from the water. Clarification must usually be assisted by the use of flocculants.

Thermal regeneration in a multiple-hearth furnace is the most common method for regenerating spent granular carbon. The development of thermal regeneration of spent powdered carbon has only recently been vigorously pursued (20,21,49,50,51). Disadvantages in regeneration of powdered carbon, compared to granular carbon, lie in the difficulty of dewatering the carbon before regeneration and in high carbon losses during thermal regeneration. No commercial system was in existence for regenerating powdered carbon, hence powdered carbon was considered as a single-use material in this evaluation.

The purchased cost of powdered carbon is substantially lower than that of granular carbon $0.085/lb. vs. $0.25-0.30(at the time of this study).

The conventional choice between the granular and powdered carbon systems for a specific application is based on an evaluation of several technical and economic factors.

Usually, the use of powdered carbon is favored when the carbon consumption is low due to low liquid volume and/or low dosage requirements (e.g. due to low contaminant concentration). Granular carbon would be favored where countercurrent adsorption is advantageous, and where the separation of a powdered carbon from the liquid being purified would present a problem. An economic evaluation must take into consideration the capital and operating costs associated with single-use powdered or granular carbon and with regenerative use of granular carbon. The latter would require the higher capital investment, but operating cost for make-up carbon would be lower.

As a third choice, St. Regis suggested a counter-current contacting system that uses a fine activated carbon of a size intermediate between powdered and standard granular carbon. A preliminary engineering assessment of this system (dubbed FACET) indicated that it combines some of the advantages of both conventional systems. The FACET system is shown schematically in Figure 6 (Section VI) as a three-stage countercurrent contacting system. A patent (41) has since been issued on this process.

Carbon size and concentration are chosen such that contact time requirements are short, while the size is large enough to provide fact settling without the assistance of flocculating agents. Therefore, FACET permits use of simple stirred tanks as contactor-settlers and avoids the need for preclarification of the water commonly required in granular adsorption systems to prevent column pressure build-up and avoids the need for frequent back-washing. Present indications are that a suitable particle-size range for FACET is about 100 to 250 microns (140 to 60 mesh). The FACET particle size is believed to be large enough to permit use of a standard multiple-hearth furnace for regeneration. The FACET process is discussed further in Section VI.

The choice among the three carbon systems as applied in this project is influenced by the proposed production of activated carbon at the mill for the treatment of mill effluent. Such mill-site production of carbon makes all three types of carbon available at a substantially lower cost and also at a smaller cost differential between granular, FACET, and powdered carbon.

Moreover, another dimension is added to the economic evaluation since carbon cost depends not only on type of carbon but on production volume. The latter is very materially dependent on whether the carbon is discarded after use or is regenerated.

As a result of this preliminary evaluation of alternative carbon systems, it appeared that all three systems should be further evaluated in the economic estimate.

ORDER OF MAGNITUDE COST ESTIMATES

Bases of Cost Estimates

Costs of equipment and overall plant costs for primary clarification, bio-oxidation, lime treatment, and carbon adsorption were obtained primarily from references 17 and 23-34. Additional sources of cost data were Infilco, Eimco, and St. Regis' internal sources. Most of the reference data on activated carbon systems are based on municipal effluent treatment.

The estimates are of the order-of-magnitude type which might have inaccuracies of 20% to 40%. Allowances were made in the capital costs for installation, engineering, and contingencies. Most capital costs were based on overall plant costs from curves or from similar plants with the cost adjusted to the desired flow rate by suitable values of capacity-cost exponents.

St. Regis Mill A total mill effluent, on which the laboratory tests were based, had a flow rate of 38 mgd, which included about 20 mgd of cooling water. Even though the flow without the cooling-water dilution would have been only 18 mgd and would have contained about twice the measured color and TOC concentrations, cost estimates were based on the 38 mgd flow because the lab data were based on this diluted flow. The average composition of this stream was 140 mg/l TOC, 1000 CU, 130 mg/l BOD, and pH 8.6.

The average composition of the St. Regis Mill C total mill effluent during the lab program was 640 mg/l TOC, 4450 CU, and pH 9.9. The color was abnormally high because of mill upsets during this period. The average flow rate was 15.3 mgd.

A limited dosage lime process (1000 mg/l CaO) similar to that used at Interstate Paper Company's Riceboro Mill (5,18) was used in these estimates. The amounts of TOC and color reduction by lime treatment that were used in these estimates are those obtained in the lab program with a dosage of 5000 mg/l CaO which gives about the same color reduction as a dosage of 1000 ppm. The capital costs for lime treatment include lime slaking, reactor-clarifier, carbonation, $CaCO_3$ clarifier, and sludge filters, but do not include any portion of the capital and operating costs of lime calcination.

The TOC reductions by bio-oxidation used in the estimates were 140 to 66 mg/l TOC for Mill A and 640 to 140 for Mill C, which were the reductions obtained in the laboratory experiments. It was assumed that the bio-oxidation would be carried out in mechanically aerated basins with a retention time of 10 days.

Three carbon treatment processes were considered: powdered carbon (about 10 micron average particle size), fine-carbon FACET system (100 to 250 micron particle size to 140 x 60 mesh), and granular carbon which is used in a fixed bed. Carbon dosage estimates were based on laboratory results with Westvaco Aqua Nuchar powdered carbon. The dosage used in these estimates was that required to reduce the color to 100 color units and TOC to 50 mg/l plus 50% excess carbon to allow for incomplete equilibration. Water with these values of color and TOC is considered satisfactory for general plant reuse.

The influence of the price of carbon on treatment costs was determined by assuming prices of $0.02, $0.085, and $0.27 per pound of carbon. The price of commercially available powdered carbon was $0.085/lb and that for granular carbon was $0.27/lb at the time of these estimates.

Charges related to fixed capital are included in operating costs on the basis of 16-year, straight line depreciation (6.25% of TCI/year), plus a total of 12% of TCI/year for repair, maintenance, taxes, and interest charges. General administrative overhead (GAO) was assumed to be 75% of labor costs plus 1.5% of TCI/year.

Pertinent operating conditions are given in Tables 13, 14, and 15 for each estimate, along with results of the cost estimates.

Results of Estimates

Overview -

Tables 13 and 14 present a summary of the conditions and cost data of the estimates prepared. The presentation in Table 15 is less detailed and shows a wider range of combinations including those of Tables 13 and 14.

Estimates A-2, A-11, and A-3 in Table 13 represent the three treatment sequences under consideration, using granular carbon adsorption. The effect of capital and operating costs on treatment system selection will be discussed first. The influence of carbon cost on capital and operating costs and indirectly on treatment system selection will be discussed subsequently.

Capital Investment -

In terms of capital investment, the primary/lime-carbon system (A-11) represents the lowest cost, mainly because of the significantly lower cost of the carbon adsorption and regeneration portion of the total system. The primary-bio-carbon system (A-3) requires the highest capital investment.

Table 13. ORDER-OF-MAGNITUDE COST ESTIMATES FOR VARIOUS TREATMENTS OF TOTAL MILL EFFLUENT FROM MILL A; EFFLUENT: 140 mg/1 TOC, 1000 CU

Estimated No. Treatments	A-2 Primary- granular carbon			A-11 Primary/lime- granular carbon			A-3 Primary-bio- granular carbon		
Effluent	Mill A			Mill A			Mill A		
Flow, mgd.	38			38			38		
Carbon treatment, type	gran.			gran.			gran.		
Dosage, lb/kgal	5.0			1.42			4.3		
Carbon conc'n., lb/ft^3	25			25			25		
Retention, hours, carbon	950			950			950		
water	1			1			1		
Carbon regeneration	yes			yes			yes		
Final filter	no			no			no		
Treated water comp'n: TOC, mg/1	50			50			50		
Color, CU	100			100			100		
Capital costs, $ million									
Price of carbon, $/lb	0.02	0.085	0.27	0.02	0.085	0.27	0.02	0.085	0.27
Primary	2.5	2.5	2.5	-	-	-	2.5	2.5	2.5
Bio-oxidation	-	-	-	-	-	-	3.6	3.6	3.6
Primary/lime treatment	-	-	-	4.0	4.0	4.0	-	-	-
Filters	-	-	-	-	-	-	-	-	-
Carbon contactors									
Carbon dewatering	6.3	6.3	6.3	2.8	2.8	2.8	5.4	5.4	5.4
Carbon drying & regeneration									
Carbon in system	0.1	0.6	2.0	0.1	0.3	1.1	0.1	0.5	1.7
Total cost of investment (TCI)	8.9	9.4	10.8	6.9	7.1	7.9	11.6	12.0	13.2
Operating cost, $/kgal									
Amortization @6.25% TCI/yr	0.040	0.042	0.049	0.031	0.032	0.036	0.052	0.054	0.059
R&M, tax, int.@12% TCI/yr	0.077	0.081	0.094	0.060	0.061	0.068	0.100	0.104	0.114
Labor + GAO	0.026	0.026	0.026	0.034	0.034	0.034	0.036	0.036	0.036
Elec. (0.5¢kwh)& gas (35¢MMBTU)	0.010	0.010	0.010	0.004	0.004	0.004	0.009	0.009	0.009
Coagulants	0.005	0.005	0.005	-	-	-	0.010	0.010	0.010
Make-up carbon (5%)	0.005	0.021	0.067	0.001	0.004	0.013	0.004	0.019	0.059
Lime (1000 mg/1CaO)@ $16/t	-	-	-	0.067	0.067	0.067	-	-	-
Total operating costs	0.163	0.185	0.251	0.197	0.202	0.222	0.211	0.232	0.287

Table 14. ORDER-OF-MAGNITUDE COST ESTIMATES FOR VARIOUS TREATMENTS OF TOTAL MILL EFFLUENTS FROM MILLS A AND B

Mill A: 140 mg/l TOC, 1000 CU,; Mill B: 640 mg/l TOC, 4450 CU

Estimate No. Treatments	A-8 Primary- fine carbon		A-6 Primary- powd. carbon		A-10 Primary/lime- powd. carbon		C-2 Primary- gran. carbon		C-3 Primary- powd. carbon	
Effluent	Mill A		Mill A		Mill A		Mill B		Mill B	
Flow, mgd.	38		38		38		15.3		15.3	
Carbon treatment, type	fine		powd.		powd.		gran.		powd.	
Dosage, lb/kgal	13		13		6.9		12.5		36	
Carbon conc'n., lb/ft^3	6		0.1		0.05		25		0.3	
Retention, hours, carbon	100		1.5		2		950		1.5	
water	1		1		2		1.5		1	
Carbon regeneration	yes		no		no		yes		no	
Final filter	sand		sand		sand		no		sand	
Treated water comp'n: TOC, mg/l	50		50		50		50		50	
Color, CU	100		100		100		100		100	
Capital costs, $ million										
Price of carbon, $/lb	0.02	0.085	0.02	0.085	0.02	0.085	0.02	0.085	0.02	0.085
Primary	2.5	2.5	2.5				1.5	1.5	1.5	
Bio-oxidation	-	-	-		-		-	-	-	
Primary/lime treatment	-	-	-		4.0		-	-	-	
Filters	1.7	1.7	1.7		1.7		-	-	0.8	
Carbon contactors	0.8	0.8	1.5		0.5		3.4	3.4	1.0	
Carbon dewatering	0.5	0.5	0.8		0.5				0.8	
Carbon drying & regeneration	1.2	1.2	-		-				-	
Carbon in system	negl.	0.2	negl.		negl.		0.1	0.5	negl.	
Total cost of investment (TCI)	6.7	6.9	6.5		6.7		5.0	5.4	4.2	
Operating cost, $/kgal										
Amortization @6.25% TCI/yr	0.030	0.031	0.029	0.029	0.030	0.030	0.056	0.060	0.046	0.046
R&M, tax, int.@12% TCI/yr	0.058	0.059	0.056	0.056	0.058	0.058	0.104	0.112	0.089	0.089
Labor + GAO	0.035	0.035	0.036	0.036	0.025	0.025	0.031	0.031	0.046	0.046
Elec.(0.5ckwh)& gas(35cMMBTU)	0.047	0.047	0.020	0.020	0.001	0.001	0.010	0.010	0.020	0.020
Coagulants	-	-	0.010	0.010	0.005	0.005	0.010	0.010	0.030	0.030
Make-up carbon*	0.013	0.055	0.260	1.100	0.138	0.590	0.012	0.053	0.720	3.05
Lime (1000 mg/l CaO)@ $16/t	-	-	-	-	0.067	0.067	-	-	-	-
Total operating costs	0.183	0.227	0.411	1.25	0.324	0.776	0.223	0.276	0.95	3.28

* (5% for A-8, C-2; 100% for A-6, A-10, C-3)

Table 15. SUMMARY OF CONDITIONS OF TREATMENT AND ESTIMATED CAPITAL AND OPERATING COSTS FOR VARIOUS TREATMENTS OF TOTAL MILL EFFLUENT FROM MILLS A AND B

Cost Estimate	Primary Clarif'n	Bio-oxid'n	Lime	Activated carbon			Final filtration	Capital cost $million[b]	Operating Cost		
				powd.	fine[a]	gran.			$/kgal[b]	$/kgal[c]	$/kgal[d]
Mill A total mill effluent											
1	x	x	-	-	-	-	-	6.1	0.12[e]	0.12[e]	0.12[e]
2	x	-	-	-	-	R	-	8.9	0.16	0.19	0.13
3	x	x	-	-	-	R	-	11.6	0.21	0.23	0.17
4	x	-	x	-	-	-	-	5.5	0.17[f]	0.17[f]	0.17[f]
5	x	-	x	-	-	R	-	8.3	0.23	0.23	0.17
6	x	-	-	NR	-	-	x	6.5	0.41	1.25	1.19
7	x	-	-	-	75,R	-	x	7.4	0.19	0.24	0.18
7A	x	-	-	-	75,NR	-	x	6.2	0.37	1.20	1.14
8	x	-	-	-	150,R	-	x	6.7	0.18	0.23	0.17
9	-	-	x	-	-	-	-	4.0	0.14[f]	0.14[f]	0.14[f]
10	-	-	x	NR	-	-	x	6.7	0.32	0.78	0.72
11	-	-	x	-	-	R	-	6.9	0.20	0.20	0.14
Mill C total mill effluent before oxidation pond											
1	x	x	-	-	-	-	-	3.5	0.16[g]	0.16[g]	0.16[g]
2	x	-	-	-	-	R	-	5.0	0.22	0.28	0.22
3	x	-	-	NR	-	-	x	4.2	0.95	3.28	3.22

[a] Average particle size in microns
[b] Based on minimum price of carbon - $0.02/lb
[c] Based on intermediate price of carbon - $0.085/lb
[d] Same as c, but incl. $0.06/kgal credit for reusable water
[e] Product water contains 570 CU
[f] Product water contains 63 mg/l TOC
[g] Product water contains 140 mg/l TOC, 2000 CU

R - regenerated
NR - not regenerated

Compared to the primary-carbon system, the addition of a biological treatment system requires a substantial added investment while not substantially reducing the investment requirement in the carbon part of the treatment sequence. Thus, when aiming at a reuse treatment system for new mill design, the primary/lime-carbon and the primary-carbon sequences appeared to be the logical first and second choices for further development, based on capital cost estimates.

However, when aiming at a reuse treatment sequence adaptable as a modification for an existing mill with a biological oxidation system, the choice would appear to become much more complex. It would include the following options: continued operation of existing facilities, with addition of a carbon system; shut-down of biological oxidation, with addition of a carbon system; shut-down of biological oxidation, addition of a lime treatment system including modification of the existing primary treatment, and addition of a carbon system. Based on the limited cost detail on individual steps of the three treatment sequences presented in Table 13 the mill system modification most closely represented by the primary-bio-carbon sequence could represent the economical choice and thus appeared to merit further development.

An elimination of any one of these three treatment sequences thus did not appear warranted on the basis of the capital investment comparison considering the objective of assuring broadest utility and applicability of successful development of new treatment systems to both new and existing mills.

Operating Cost -

Comparing operating costs, including fixed costs based on capital investment, at a carbon cost of $0.02 or $0.085/lb., the primary-carbon system represents the lowest cost system. Total operating costs for the primary/lime-carbon system are 15% above the primary-carbon system, and the primary-bio-carbon system is yet 10% higher in cost. These differences are within the accuracy of these estimates and at most indicate a possible cost trend. In the case of an existing mill with a biological oxidation system, and where that system is already fully or partially depreciated, the primary-bio-carbon system would again tend to compare more favorably. Thus on the basis of operating cost, using mill-site produced carbon at up to about $0.085/lb., no justification was seen to eliminate any of the sequences from further development under the objectives of this program.

Carbon Cost -

The fraction of total capital investment (TCI) represented by the carbon inventory merits closer inspection. It is seen to be an insignificant factor at a carbon cost of $0.02/lb., and a fairly low fraction (about 5%) of TCI at a carbon cost of $0.085/lb. However, at a carbon cost of $0.27/lb. (equivalent to purchased carbon), carbon inventory amounts to 13%-19% of TCI. Assuming successful development of mill-site carbon production at a cost of $0.02-.085/lb. carbon, system selection is essentially insensitive to the capital investment cost aspect of the carbon inventory. Carbon costs above the stated range tend to favor the primary/lime-carbon treatment sequence.

Total operating costs, including fixed costs based on capital investments, of all three sequences vary with carbon cost for two reasons: (a) make-up carbon represents a (variable) direct operating cost item; (b) the initial carbon charge (inventory) represents a (variable) capital investment cost item. However, the operating cost of the primary/lime-carbon system is relatively insensitive to carbon cost. Over the range of carbon prices examined ($0.02 to $0.27/lb.), the operating cost of the primary/lime-carbon system increases by only 15%, while the operating cost of the primary-carbon system increases by 54%. This makes the primary/lime carbon system the less costly system to operate with (purchased) carbon at $0.27/lb.

The estimated operating costs of the primary/lime-carbon system, using purchased carbon at $0.27/lb., do not compare too unfavorably with the primary-carbon system using mill site-produced carbon at $0.085/lb. or less. The lower indicated investment cost of the primary/lime-carbon system using purchased carbon may offer sufficient reason in a specific case to give it serious consideration in comparison with systems offering lower operating costs.

Carbon Adsorption Systems

Table 14 brings out the effect of different carbon systems on capital and operating costs. It should be noted that the estimates in Table 14 were prepared only for two different carbon costs of $0.02 and $0.085/lb.

The FACET system is represented by estimate A-8. It shows a moderate increase in direct operating costs over the granular carbon system A-2 (Table 13). This increase is due to higher estimated carbon dosage and correspondingly higher make-up requirements and to higher regenerating utility costs. Comparing the capital cost estimates A-8 and A-2, the potentially significantly lower TCI of the FACET system is observed. This lower capital requirement would appear to make the

FACET system an attractive alternative to the granular carbon system, if the lower costs can be substantiated on the basis of further development and subsequent cost estimates.

The effect of using powdered carbon in the primary-carbon sequence with no regeneration of the carbon is indicated in estimate A-6, and may be compared with the corresponding granular carbon system estimate A-2. Operating costs for A-6 are higher, even at the lowest assumed carbon cost of $0.02/lb, due to higher carbon requirements in the absence of carbon regeneration. On the other hand, the TCI for A-6 is lower in the absence of investment costs for carbon regeneration. However, non-competitive operating costs of the powdered carbon system provided a basis for ruling it out from further development.

A-10 is an estimate of the powdered-carbon version of the primary/lime-carbon sequence. A comparison with A-11 (primary/lime-granular carbon) shows no capital cost advantage of A-10, while operating costs are substantially higher than A-11, even at the lowest carbon cost of $0.02/lb, and in spite of the relatively low carbon dosage required. Based on this and on the preceding comparison of A-6 with A-2, it appeared that further development of a powdered, non-regenerative carbon system was not warranted.

Effluent Contaminant Concentration -

Estimate C-2 in Table 14 is for primary-carbon treatment of Mill C total mill effluent which is more concentrated than that of Mill A but has a lower daily flow. In comparison with estimate A-2 in Table 13, C-2 shows a higher operating cost primarily because of higher fixed costs per unit volume of water and to a lesser extent because of increased carbon dosage. Estimates for treating Mill C effluent by the other two sequences were not prepared, since it was unlikely that the pilot plant system selection would have been influenced by these estimates.

Estimate C-3 emphasizes the unattractiveness of a non-regenerative powdered carbon system as discussed in conjunction with A-6 and A-10. The higher carbon dosage required in C-3 makes it comparatively even less attractive.

Comparison of Reuse Systems with Other Systems -

The comparison of treatment systems in Table 15 indicates that the use of carbon treatment (either granular or FACET) might be only slightly more costly than biological oxidation, A-1, Table 15. Carbon treatment, and in some situations lime treatment, would provide a water suitable for reuse. In general, primary-bio treatment will not reduce the color sufficiently and primary-lime will not reduce the TOC, and perhaps color, sufficiently for reuse in the mill, and will not reduce BOD sufficiently for discharge to rivers in the future. The cost estimates indicate that lime treatment would be 15% higher than bio-oxidation. However, firm design and cost data were not available for the lime treatment process and there was some doubt as to the reliability of the values used in the estimation of the costs for lime treatment.

FINAL SELECTION OF TREATMENT SEQUENCES AND CARBON ADSORPTION SYSTEMS

The final selection of treatment sequences to be piloted was as follows:

(1) Primary-carbon
(2) Primary/lime-carbon
(3) Primary-bio-carbon

(The actual execution of the primary/lime carbon sequence in the pilot plant used a holding pond to smooth out concentration variations and inadvertently acted as a primary clarifier before lime treatment.) An examination of the economics and consideration of other factors did not provide a basis for eliminating any of the three treatment sequences considered. This program's orientation towards both new mills and existing mills precluded the elimination from development, on economic grounds, of the primary-bio-carbon system, as discussed previously. Such elimination, moreover, would require strong justification considering the fact that the primary-bio-carbon system has the advantage of minimum departure from established technology.

In the final selection of carbon systems within the above treatment sequences, the single-use powdered carbon system was eliminated from further development because of its comparatively high cost. The remaining two systems; i.e., granular carbon and FACET, both indicated certain comparative economic and technical advantages. In terms of cost, the granular system indicated somewhat lower total operating cost, while the FACET system indicated lower capital investment. From a cost estimate reliability standpoint, the granular carbon system estimate was probably a more reliable one than that for the FACET system because of the availability of substantial reference material for the granular carbon systems compared with the conceptual status of the FACET system.

From the technical standpoint, the FACET system would appear to offer a better chance of avoiding certain problems that could develop in the operation of large-scale adsorption systems. Granular carbon columns tend to develop anaerobic biological activity. In a FACET system, it would be a relatively simple matter to control anaerobic activity or take advantage of aerobic activity by the injection of air. Another problem is often caused by suspended solids, leading to plugging and the need for frequent backwashing of granular carbon columns. Suspended solids are not expected to be a problem in the FACET system. Problems of this type can only be properly assessed in a pilot plant. Design data for a more reliable capital cost estimate for a commercial system also can only be obtained on the basis of pilot plant operating data. Hence, it was considered desirable to include both the granular carbon and FACET system in the plans for the pilot plant.

SECTION VI

PILOT PLANT DESCRIPTION AND OPERATION

OBJECTIVES

A pilot plant was designed and constructed that would meet the objectives of this program: to determine the technical feasibility of the selected treatment sequences involving carbon adsorption for removal of color and TOC from unbleached kraft mill effluent, to develop suitable conditions of operation, and to provide engineering design data for commerical systems.

The pilot plant was designed so that effluent treatment by any of the following three sequences could be investigated:

Primary-carbon
Primary/lime-carbon (abbreviated lime-carbon)
Primary-bio-carbon (abbreviated bio-carbon)

Although the system selection detailed in Section V provided for inclusion of the primary/lime-carbon system, i.e., lime addition followed by simultaneous removal of lime-color bodies and settleable solids in a primary clarifier, pilot plant plans were for practical reasons developed on the basis of lime treatment following primary clarification. (A holding pond, required to smooth out concentration variations, inadvertently acted as a primary clarifier before lime treatment.) The design incorporated two carbon adsorption systems, i.e., downflow columns and FACET, and provided for simultaneous operation of both, resulting in a total of six treatment options.

DESCRIPTION OF PILOT PLANT

Location

The pilot plant was located alongside the effluent ditch from the St. Regis Pensacola No. 2 Mill that normally produces 620 tons of unbleached pulp per day from a charge of 25% hardwood and 75% southern pine. This mill, built in 1948, uses batch digesters and produces mainly bag paper. The Pensacola mill effluent was selected for use in the pilot plant because this mill is typical of the more prevalent older pulp and paper mills. In addition, the Pensacola location affords the opportunity of testing a wide range of individual and combined effluents including bleach effluents from the No. 1 Mill.

Basis for Design of Pilot Plant

The pilot plant was designed to treat 30 gpm of mill effluent in the bio-oxidation and lime treatments, 15 gpm in the carbon columns, and 15 gpm in the FACET system. These flows accommodate the desire for large flows to provide reliable commercial design data and yet are small enough to keep equipment and operating costs within reasonable limits. The 30 gpm capacity of the bio and lime units gave sufficient flow for side-by-side evaluations of the two carbon systems with the same feed water.

The pilot plant was designed for continuous operation seven days per week because intermittent operation would not have provided useful data for evaluation and designs. To provide operation round-the-clock, it was decided to use operators one shift per day for five days per week and to provide sufficient automatic controls and instrumentation to permit continuous operation without operator attendance during the remaining shifts, thus avoiding the cost and manpower scheduling problems connected with round-the-clock operator attendance, particularly for pilot plants.

An aeration basin (187,000 gal) was used for bio-oxidation because this method is the most commonly used method for bio-oxidation treatment of pulp mill effluents. A retention time of 4.3 days was used in designing the equilization-aeration basin. The depth of the earthen-dam rectangular aeration basin (8 ft) and the size of the floating aerators were selected to make the operation of the aeration basin typical of full-scale aeration basins.

A large amount of flexibility was incorporated in the pilot plant to permit any treatment step to be by-passed or to permit simultaneous operation of as many as three of the six treatment options.

Pilot Plant Equipment

A flow diagram of the pilot plant is shown in Figure 5. Effluent is pumped from the ditch into a basin having a volume of 187,000 gallons and providing 4.3 days retention time when operating at 30 gpm. The basin is of compacted earth construction with the interior sloping sides coated with gunnite concrete to prevent water erosion of the sides. The basin serves to dampen the wide fluctuations of impurities, which may vary as much as 6-fold within a few days. One section of the basin provides primary clarification at a rise rate of 100 gpd/ft^2 at 30 gpm. Water from the basin passes through slots in a wooden wall placed across one corner of the basin. The wall consists of vertical boards with ¼ to ½ inch spacing between boards. Only the lower one or two feet of the slots are open, the remainder is covered with plastic to minimize water circulation from the aeration section.

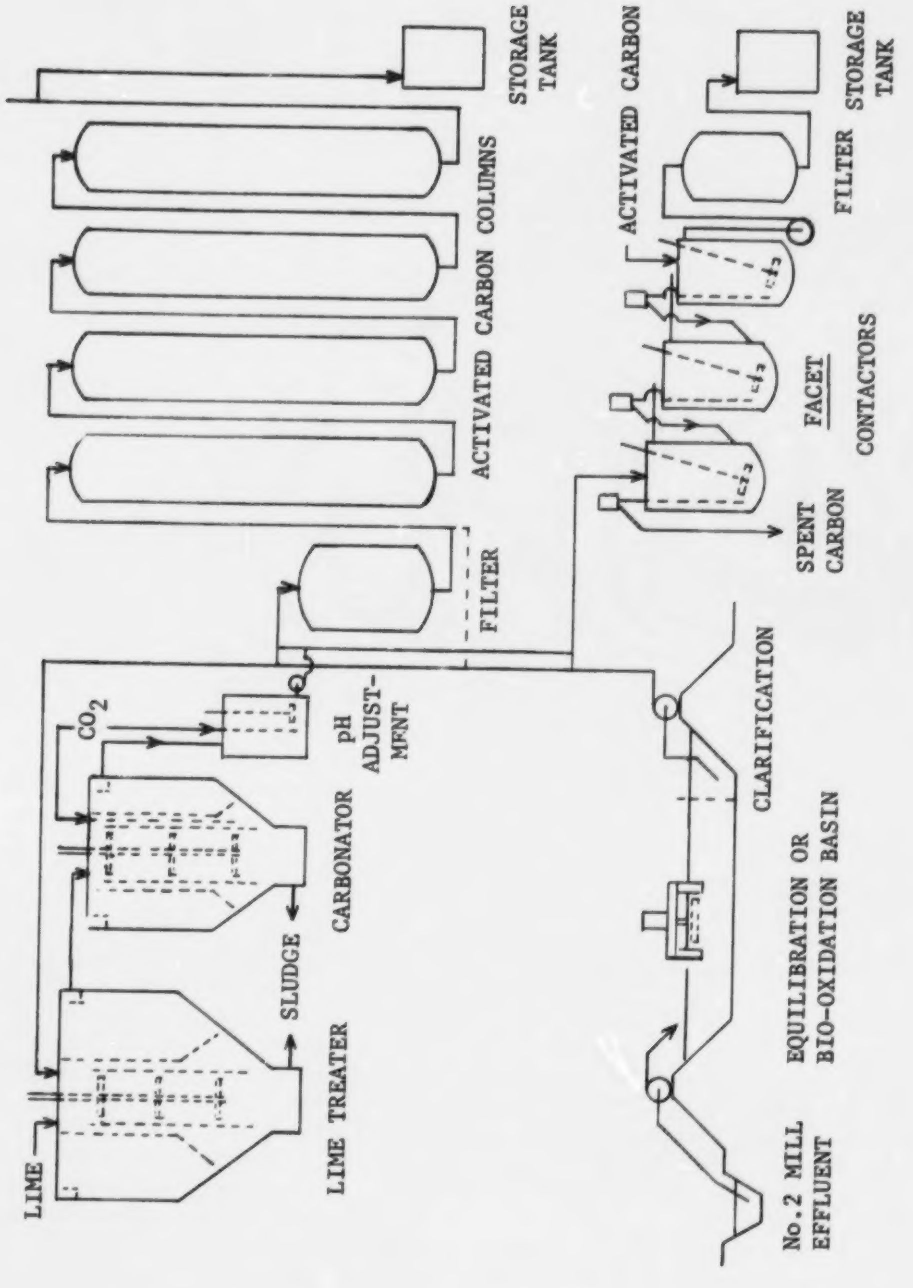

LIME
LIME TREATER
SLUDGE
CARBONATOR
CO_2
pH
ADJUST-
MENT
FILTER
ACTIVATED CARBON COLUMNS
STORAGE
TANK
No.2 MILL
EFFLUENT
EQUILIBRATION OR
BIO-OXIDATION BASIN
CLARIFICATION
SPENT
CARBON
FACET
CONTACTORS
ACTIVATED CARBON
FILTER
STORAGE
TANK

Figure 5. Effluent treatment pilot plant

The basin has a 5 hp surface aerator which is operated when biological oxidation is desired as part of the operating sequence. In that case, nutrients at normally used dosages are also fed to the basin. Further details on the basin and on each portion of the pilot plant are given in Appendix C.

Effluent from the basin is pumped either directly to one or both of the two activated carbon adsorption systems, or it is pumped to the lime treatment system and then to the activated carbon systems.

The lime treatment equipment consists of a 10 ft diameter reactor-clarifier with a 39 in. diameter center well, providing a retention time of 20 minutes in the reactor section and a clarifier rise rate of 550 gpd/ft^2 at 30 gpm. Lime addition in the reactor raises the pH of the effluent to about 12 and causes precipitation of a mixture of $CaCO_3$ and a Ca-organic floc. Lime addition is by pump from a mix tank into which hydrated lime is fed continuously from a hopper where it is slurried with about 5 gpm of recycled lime-treated effluent. A second reactor-clarifier permits carbonation of the lime treated, clarified effluent for removal of excess dissolved lime at pH 10.5. In the pilot plant,bottled CO_2 is used for this purpose. At 30 gpm, this 7.5 ft diameter reactor-clarifier provides a retention time of 27 minutes in the reaction zone and a clarifier rise rate of 1000 gpd/ft^2. A 200 gallon tank is provided for final pH adjustment with CO_2.

The lime treatment unit, the carbonation unit, the pH adjustment tank, and a 10,000 gal surge tank are located on an outdoor concrete pad. The remaining equipment items are located inside a 30 x 52 ft prefabricated steel building having a 20 ft wall height. The building also provides storage for truck-load quantities of lime and carbon.

Two activated carbon adsorption systems are provided in the pilot plant, intended for simultaneous comparative operation if desired, both at 15 gpm. One system consists of four standard downflow carbon columns, 3 ft diameter by 15 ft high, each with a carbon bed of 10 ft (1600 lb of granular carbon of 20 x 40 mesh size). At 15 gpm, each column provides 0.6 hour retention time in the carbon bed at a superficial velocity of 2 gpm/ft^2. All water connections to the columns are by means of 1½ in. hoses with quick disconnects so that any desired arrangement of series or parallel flow could be used, either up-flow or down-flow through the columns. This arrangement greatly simplified the piping, especially for backwashing.

A 4-ft diameter duomedia filter with a filter bed of 1 ft of anthracite and 1 ft of sand, supported on graded gravel, is provided for filtering the feed to the carbon systems when desired.

A second carbon system, a novel system called FACET (for Fine Activated Carbon Effluent Treatment) and subject of a U.S. patent (41), was included in the pilot plant for initial development (Figure 6). The FACET system is a multi-stage counter-current agitated system with continuous counter-current transfer of carbon and liquid from stage to stage. The tanks used in the pilot plant are sized 3 ft diameter by 5 ft high, with a mixing zone of 170 gallons and a carbon charge of 212 lb per tank at 15 g carbon per 100 ml of slurry, or 15 wt/vol %.

Water to be treated flows by gravity through the three stirred tanks in series and then to a product storage tank or is pumped through a 3-ft diameter duomedia filter and then to the product water tank. Activated carbon, which has a mesh size of 40 by 140 mesh, is fed from a feed hopper into the third FACET tank. Carbon slurry, which typically has a concentration of 15 wt/vol %, is removed from the third tank at the same rate as the carbon is fed to that tank. The carbon is thus moved counter-current to the flow of water through the second tank, through the first tank, and to a spent-carbon container.

The system endeavors to avoid some of the problems associated with the conventional granular and powdered carbon contacting systems, while combining advantages of both of these systems by using a carbon size intermediate to the standard powdered and granular classifications. Adsorption rate being inversely proportional to the square of the carbon particle diameter (12,13), the intermediate size carbon loads up to its capacity much faster than the coarser granular carbon. Although the ultimate capacities of both granular and intermediate size carbons are essentially equal, the higher adsorption rate of the intermediate size carbon results in a corresponding increase in carbon turn-over rate and a corresponding decrease in carbon inventory. Equipment size for the adsorber decreases correspondingly.

The FACET system allows close control of the quality of the treated effluent by adjustments in carbon transfer rate or carbon slurry density, or both. Continuous discharge of spent carbon permits a closer tie between regenerator capacity and average carbon throughput, eliminating costly offstream inventory of carbon. Suspended solids present in the liquid to be treated do not present a plugging problem as in the granular carbon column system, hence primary clarifiers may be omitted.

Comparing FACET to the powdered carbon system, the intermediate size carbon has a higher settling rate than the powdered carbon. This obviates the need for flocculants and substantially reduces the clarification area compared to that of a powdered carbon system (clarification area being a function of liquid flow rate and particle sedimentation rate). Use of the intermediate size carbon allows a properly

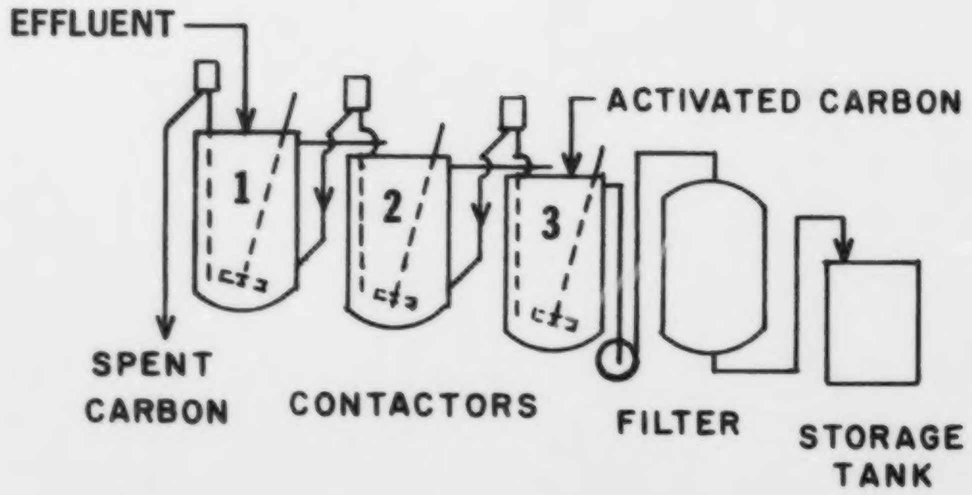

EFFLUENT
ACTIVATED CARBON
1
2
3
SPENT CARBON
CONTACTORS
FILTER
STORAGE TANK

Figure 6. FACET system

baffled agitated tank to serve as both adsorber and clarifier. As a result, equipment size as well as cost is significantly lower for the FACET system than for the powdered carbon adsorption system.

Figure 7 shows the pilot plant building, the lime-treatment equipment, and equalization basin. Figure 8 shows the carbon columns, the duomedia filter in the right foreground, and the FACET tanks in the front foreground.

Instrumentation

Instrumentation of the pilot plant is sufficient to permit continuous 24-hour operation with only one operating shift for adjustments and sample taking. Conductivity, pH, turbidity, temperature, and flow rate are recorded continuously.

Three water flow rates are automatically controlled and recorded: feed to lime treatment, feed to carbon columns, and feed to FACET carbon system. Automatic controllers are provided on the CO_2 feed lines to the carbonator reactor-clarifier and pH adjustment tank to control the pH in these tanks at a selected level. Timer controllers are provided for the sludge valves from the lime treater and the carbonator.

The monitoring of the qualities of 12 streams in the process is provided by a step programmer at the instrumentation-control center of the pilot plant. Lines from 11 sample points and a tap-water line are brought to the continuously operated sampling instruments through programmer controlled solenoid valves. The programmer opens one sample line at a time in sequence and the water from that sample point flows in series through a conductivity cell, pH measuring cell, a Hach light-scattering turbidimeter, and a Bausch and Lomb Spectronic-70 spectrophotometer for measurement of color. The signals from these four instruments and a thermocouple are conditioned and recorded on a twelve-point recorder during a five-minute measuring and printing cycle for the sample stream that is on. The stream number that is being measured is identified on the recorder. After the five-minute period on one stream, the programmer steps to the next sample stream that is to be analyzed. The programmer can be modified to permit analysis of only the sample streams of real interest, which reduces the overall cycle time. This programmed stream analysis system permits the above five important parameters to be measured and recorded during the unattended evening shifts and on weekends. When an operator is present, the stream analysis system is valuable for showing trends and rate of change which permits better control of the operation. The pilot plant was built and shake-down runs made during 1971. The total cost of the pilot plant, excluding the building, was $194,000.

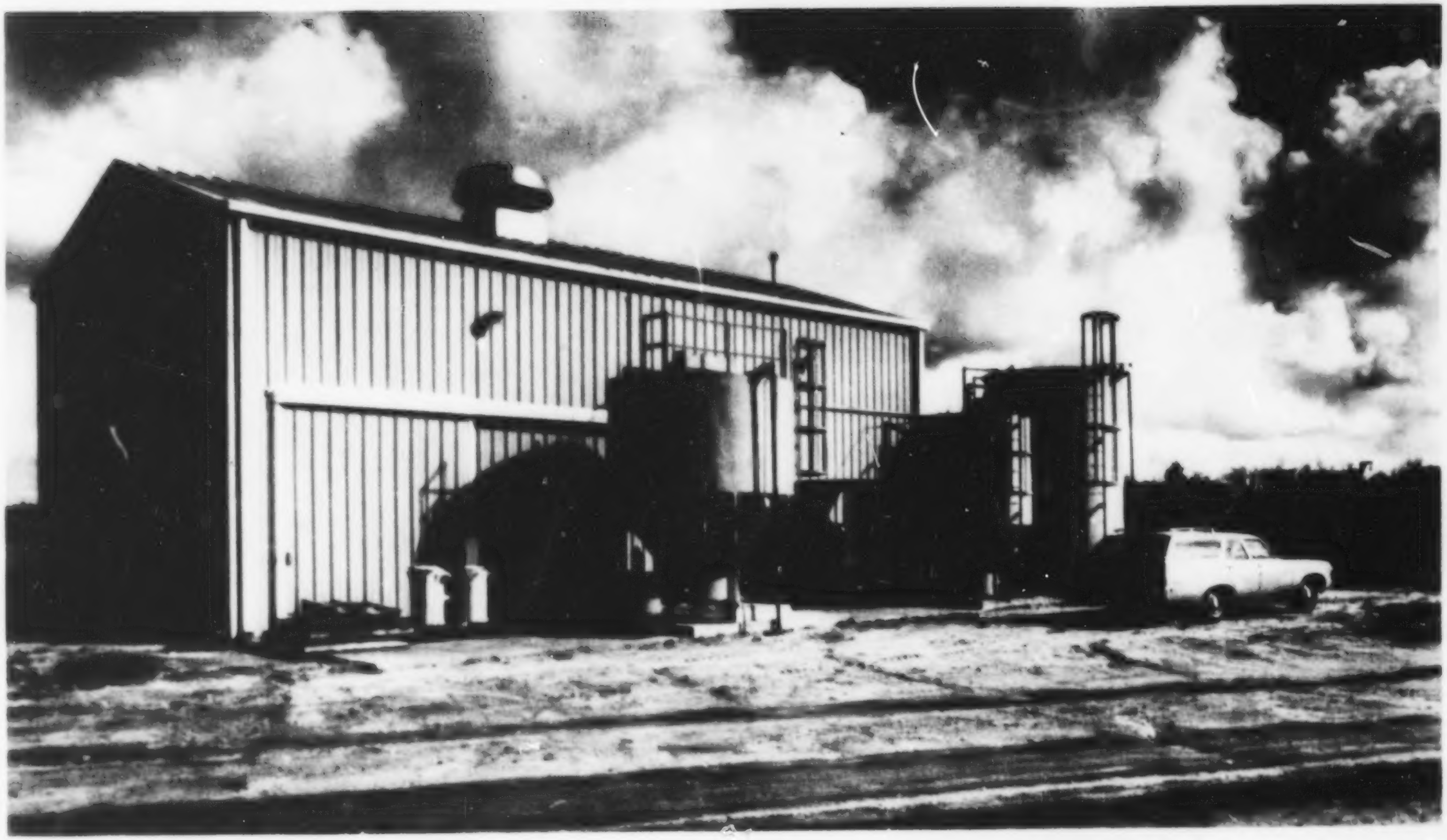


Figure 7. Exterior of pilot plant showing lime treater, carbonation tank, storage tank, and basin

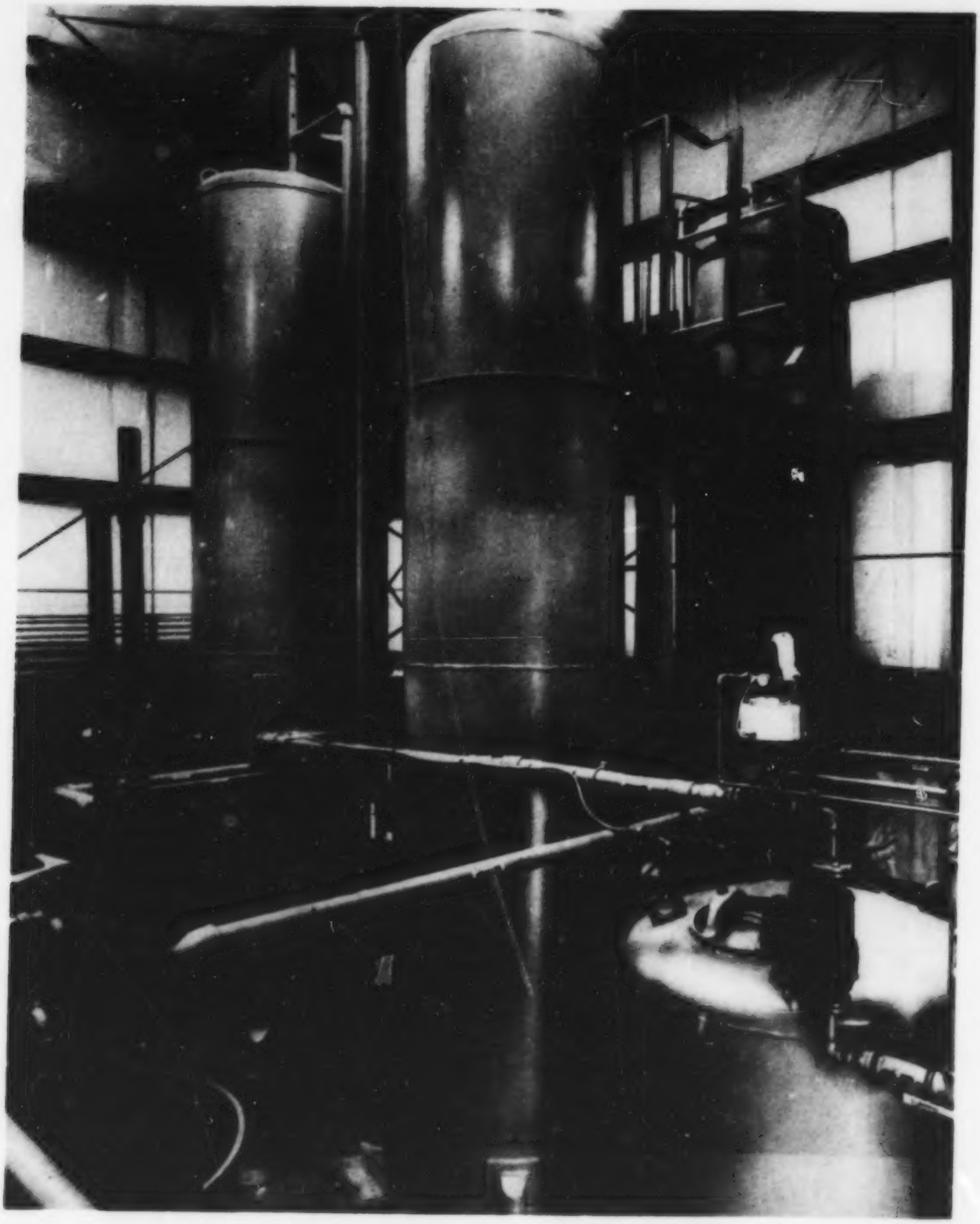


Figure 8. Interior of pilot plant with carbon columns, FACET tank (foreground) and duomedia filter (right foreground)

OPERATING PROCEDURES

The normal procedures used in operating each part of the pilot plant, and the sampling and analytical procedures are discussed in this portion of the report. Procedures that were unique to a given treatment sequence are discussed in the sections on each treatment sequence. A simplified flow diagram is given in Figure 5.

Bio-oxidation and Clarification

The operation of bio-oxidation in the aeration basin was quite simple and required little attention. Water was pumped continuously from the mill effluent ditch through a 4-mesh strainer that was placed beneath the surface of the water in the ditch. At times when there was quite a bit of fiber in the effluent, the screen would accumulate solids and would require cleaning with a brush. The water was pumped into a basin at a flow rate of about 4 gpm greater than was being used in the pilot plant. The excess water flowed through a constant-head overflow attached to the drain line from the bottom of the basin. The water being pumped from the mill effluent ditch was discharged into the basin at the end opposite the withdrawal point. The retention time of water in the basin during bio-oxidation was 6.5 days, based on a flow rate of 20 gpm. Nutrients (ammonium nitrate and phosphoric acid) were added once per day in the ratio of 2.5 lb N and 0.5 lb P for each 100 lb of BOD in the incoming water, which is the usual rate of addition in southern kraft mills. The 5 hp surface aerator was run continuously which kept the dissolved oxygen at about 6 mg/l. (A spare aerator was also placed in the basin for use if needed.)

Primary Clarification

When the operating sequence called for primary clarification without bio-oxidation, the aerator was turned off, nutrient feed was discontinued, and the aeration basin then served as an equalization basin to help level out the hourly and daily fluctuations of impurities in the mill effluent. The water from the equalization basin passed through the clarifier section of the basin and was pumped to the next treatment step.

Lime Treatment

When the operating sequence called for lime treatment, the aeration basin was again used as an equalization basin, with aeration and nutrient feed turned off, to level out impurities concentrations in the effluent. The water also passed through the clarification zone, although clarification was not called for at that point of the intended treatment sequence. Water from the clarification zone of the basin was pumped through a flow controller to the center mixing zone of the lime treater where a dilute slurry of lime was also fed continuously. Bagged hydrated lime was charged to a hopper on the feeder every one to three days. An oscillating screw feeder dropped the lime at the selected dose rate into a mixing tank to provide the slurry that was pumped to the lime treater. Water for slurrying the lime was recycled from the lime treater through a flow meter and a float valve which maintained a constant level of water in the slurry tank.

The rate of feed or dosage rate of lime was manually set at a constant value for periods of at least several days and was varied only when attempting to relate color reduction to dosage. Later it became evident that for microlime treatment, the lime dosage should be varied to maintain a constant concentration of soluble calcium. Without a suitable continuous monitor for soluble calcium, the control of dosage to maintain a constant soluble calcium content was barely satisfactory.

The mixture of lime and water in the axial cylindrical mixing chamber of the lime treater was agitated by a slow-moving multiple-arm stirrer. The water moved from the bottom of the mixing chamber upward through the clarification zone and overflowed to a pipe leading to the carbonator. Sludge that settled to the bottom of the lime treater could be discharged to the drain through a timer-controlled valve but was normally withdrawn once per day to a 50-gallon tank for measurement and sampling. Later in the program, it was found that better lime treatment was obtained by circulating sludge at about 5 gpm to the top of the mixing chamber to increase the solids content of the water in the mixing chamber.

Carbonation

The carbonator was of the same design as the lime treater except that the clarification zone had half the volume and cross-sectional area of the lime treater, which provided twice the rise rate of the lime treater. Water, which flowed by gravity from the lime treater, was treated with cylinder CO_2 in the mixing zone to remove the excess lime in the water as $CaCO_3$. The CO_2 was fed from two banks of cylinders through pressure regulators, a flow control valve, and a flow indicator to a turbine-type gas disperser placed about 4 ft below the surface of the carbonator mixing chamber. An inverted-trough CO_2 bubbler located at the bottom of the mixing chamber was used initially for admitting the CO_2 to the water but the efficiency of absorption was very poor. The turbine type of CO_2 disperser gave very good absorption efficiency. Sludge recycle to the top of the carbonator mixing chamber was later added by use of an air lift. Sludge from the carbonator was discharged once per day to the sewer.

pH Adjustment

Water from the clarification zone of the carbonator flowed by gravity to a 200-gallon tank in which CO_2 was admitted through a turbine disperser to adjust the pH to the desired level. The rate of admission of CO_2 to the carbonator and to the pH adjust tank was controlled automatically to the desired pH as measured by pH sensors in these tanks.

Carbon Column Adsorption

Water from the lime treatment unit, from bio-oxidation, or from primary clarification alone was pumped either directly to the carbon columns or through a duomedia filter and then to the columns. The duomedia filter operated quite satisfactorily if it was backwashed every one or two days for about 10 minutes at about 6 gpm/ft^2. Less frequent backwashing of the filter resulted in the formation of mud balls in the filter which were not broken up during backwashing. Backwash water was provided by well water stored in the 10,000 gal surge tank.

Each column was charged with 1600 lb of Atlas Darco 20 x 40 mesh activated carbon for all runs, which gave a bed depth of 10 ft and a bed volume of 70.7 ft^3. The columns were operated in the down-flow mode during all of the pilot plant runs. The water from the bottom of the first column flowed through the hose inter-connections to the top of the second column, and so forth, for as many columns as were to be used. The water from the final column flowed through a vertical riser pipe to an overflow equal to the height of the columns. This overflow device insured that the columns always remained full of water. The water pressure after each column was measured and the pressure drop across each column was checked several times each day and was recorded daily. At the relatively low flow rates used (0.7 to 2.1 gpm/ft^2), the pressure drop across all four columns remained at low values of 2 to 8 psi. Sample taps were available on each column at 2-ft intervals, but samples for analysis were normally obtained only after each column.

The columns were backwashed every other day with well water stored in the 10,000 gal surge tank at 35 gpm (5 gpm/ft^2) for 20 min. Before the backwash was started, compressed air was admitted to the bottom of each column to thoroughly agitate the carbon bed and break up any mud layer that might be forming on the top of the carbon bed. The backwash water was discharged to the sewer but, in a commercial plant, it would be clarified and reused for backwashing or added to the feed to the columns.

When the quality of the product water from the columns became poorer than the selected limits, the first column was removed from the system and a column with a fresh charge of carbon was added as the last column. The second column then became the lead column. The carbon from the column that was removed from operation was discharged as a slurry by opening a 6-in hand-hole at the base of the carbon bed (top of the sand-gravel support bed). The spent carbon was discarded. Fresh carbon from bags was recharged to the column through a manhole at the top after water was added to the column. Bagged carbon was hoisted by an electric hoist to a charging platform at the top of the four columns.

FACET Adsorption

Water from the basin or from lime treatment was pumped through a flow control valve to the first of the three FACET contacting tanks. The water flowed by gravity through the three tanks to a product storage tank or through a pump and duomedia filter. The speed of each of the slow-speed agitators in the FACET tanks was adjusted to barely keep all of the carbon suspended.

Carbon to FACET (Atlas Darco 40 x 140 mesh XPT activated carbon) was charged to the feed hopper from bags and fed by a feeder and vibrating conveyor to the third FACET tank. The usual rate of carbon addition for treating 10 gpm of lime-treated water was only about 2-4 lb/hr. The carbon was moved at this same rate through the three tanks countercurrent to the water flow, while the concentration of carbon in each tank was maintained at the desired level (10-15 wt/vol %) by adjusting the flow of carbon from each tank. The carbon was transferred as a slurry from tank to tank by means of air lifts which performed reliably. Originally, we tried rotary-vane pumps having neoprene impellers for transferring the carbon slurry but these were not satisfactory. The solids concentration in each tank was measured several times during the day shift, and the rate of transfer from each tank was adjusted to give the desired solids concentration by adjusting air flow to the air lift. Spent carbon from the first FACET tank was collected, drained of water, weighed, and sampled for determination of moisture content.

As indicated in Figure 6, baffles were provided in each tank to provide a clarification zone at the top of each tank so that no carbon would be carried by the water to the succeeding water treating tank. The baffles were inclined at an angle of 45^{o} to allow the settled carbon to slide back into the agitated zone. These baffles had sufficient openings around the edges that some turbulence from the mixing zone persisted into the clarification zone which allowed some of the carbon to be carried by the water in the wrong direction. This lack of good clarification was particularly troublesome in the third FACET tank because some of the fresh carbon was lost from the system in the product water. The rise rate in this zone was 1.4 gpm/ft^2 at 10 gpm, which allowed the 140-mesh particles to remain in the tank since they settled at a rate of about 18 ft/hr which is equivalent to 2.2 gpm/ft^2.

SAMPLING AND ANALYTICAL PROCEDURES

Samples were taken once per day during most of the pilot plant runs. Even though most of the properties of the water at each stage of the treatment varied only slightly during a 24-hour period, some streams were sampled more frequently if the changes were more rapid or if a special run was being made. The previously described automatic sensing and recording of pH, conductivity, temperature, color, and turbidity provided a constant readout of these properties for any number of sampling points up to twelve.

Samples taken each day were analyzed in the research laboratory using the procedures and analytical equipment described in Appendix B. The properties determined in the analyses and the usual frequency of analysis are given in Table 16. In normal operation, we sampled and analyzed seven streams during operation of the bio-carbon sequence, six during the primary-carbon sequence, and eight during the lime-carbon sequence. When the FACET unit was operated, an additional 3 or 4 samples were analyzed. Most of these were analyzed daily but some much less frequently, as indicated in Table 16.

Table 16. PROPERTIES OF WATER ROUTINELY MEASURED

Property	Frequency of analysis per week
Color, FPCU (paper filter)	7
MPCU (0.8 micron Millipore filter)	7
CU (standard color)	7
TOC (paper filter)	7
TIC (paper filter)	7
pH	7
Temperature	7
Turbidity	1-7
Conductivity	2-7
Suspended solids	1
Total solids	1
Total dissolved solids	1
BOD-5	1
Sulfate	1
Calcium	7
Volatile neutral compounds	1
Volatile organic acids	1
Foam tendency	1
Adsorption isotherms after each step of treatment	1 per month
Metals(Mg, Fe, Na, K, Al, Cr, Ni)	about 2 per month
Solids in lime sludge	1
Calcium in lime sludge	1

Based on pilot plant experience, it was found desirable to determine the parameter of "color" not only by the industry standard APHA-NCASI method but also by modified procedures which measure apparent color. In the APHA-NCASI method, color is measured at 465 nm on a spectrophotometer after adjustment of pH to 7.6 and filtration through a 0.8 micron Millipore filter. All values reported in this report unless otherwise designated were obtained by this method, and are reported as "CU". One modified procedure involved 0.8 micron Millipore filtration prior to adjustment to pH 7.6. (Used after lime treatment, this procedure ensures more complete removal of suspended solids.) Another modified procedure consisted of measuring color after filtration through a Whatman No. 2 filter paper and adjustment to pH 7.6, referred to as "7.6 FPCU". A third modified procedure consisted of measuring color after filtration through Whatman No. 2 filter paper without pH adjustment, noted as "FPCU". A fourth modified procedure consisted of measuring color after filtration through an 0.8 micron Millipore filter without any pH adjustment, noted as "MPCU".

The 7.6 FPCU for the different treatment sequences were higher than the standard colors by the following factors: bio-carbon, 2.0; primary-carbon, 1.7; lime-carbon, 1.7. Apparent colors (FPCU) measured with pH adjustment (in the pH range of approximately 8 to 11.5) were higher than pH-adjusted colors by a factor of about 2.0.

The color of effluents from pulp and paper mills decreases as the pH is reduced from pH 12 to pH 7.6, which is the desired pH for discharge to streams. As the pH is further reduced the color decreases and then drops rapidly at pH 4 and below, at which point the lignin compounds start to precipitate from solution and are most completely precipitated at pH of about 2.

The ratios of FPCU/MPCU and also FPCU/TOC were used to indicate the concentration of large colloids and agglomerated color bodies in the water that passed through a paper filter but were retained by the 0.8 micron Millipore filter.

MANPOWER REQUIREMENTS

The operation of the pilot plant normally required one operating engineer, one operating technician, and one analytical technician for 40 hr per week. Analysis of data, planning, supervision of supporting laboratory studies required 40 hr per week of an experienced development engineer. Maintenance, especially for the pH controllers and continuous water analyzers, required a craftsman about 8 hr per week.

SECTION VII

OPERATING RESULTS:

PRIMARY CLARIFICATION AND BIO-OXIDATION

BIO-OXIDATION

The bio-carbon treatment sequence was the first to be evaluated in the pilot plant after shake-down runs were made to check out each treatment stage. The procedure used in operating the aeration basin for biological oxidation was discussed in Section VI.

The aeration basin was operated continuously from December 1, 1971 to March 18, 1972, with the primary purpose of providing bio-treated water as feed to the carbon columns that would be typical of bio-treated water from aeration basins used by a large number of pulp and paper mills. The bio-carbon sequence of treatment would provide operating and cost data that could be used by those mills to evaluate the treatment of the water from their aeration basins by carbon adsorption to provide water suitable for reuse in the mill.

The rates of removal by bio-oxidation of BOD and TOC in the basin were only slightly less than those obtained by aeration basins in the pulp and paper industry. At the usual flow rate of mill effluent through the basin of 20 gpm, the retention time in the 187,000-gal basin was 6.5 days. The 5-hp surface aerator maintained an average dissolved oxygen content of 6 mg/l. The temperature of the incoming water was about 115°F, and the average temperature in the basin was 74°F. Average results from bio-oxidation are given in Table 17 for the period of February 4, 1972 to March 11, 1972, which was the period used for evaluating the results from the bio-carbon sequence.

Table 17. BIO-OXIDATION AND CLARIFICATION FOR PERIOD OF 2/4/72 to 3/11/72 AT FLOW RATE OF 20 GPM

	To basin	From basin	Percent removal
BOD, mg/l	278	69	75
TOC, mg/l	278	139	50
Color, FPCU	1610	1329	17
MPCU	1330	871	35
CU	950	810	15
pH	10.2	8.6	-
Temperature, °F	116	74	-
Conductivity, micromhos	1580	-	-
Turbidity, JTU	34	23	32
Suspended solids, mg/l	422	202	52
Methanol mg/l	35	4.1	88
Acetaldehyde, mg/l	9	10	0

During this test period, the average removal of BOD was 75%, the removal of TOC was 50%, and the removal of standard color was 15%. For comparison, the removals in the aeration basins treating the total effluent from the Pensacola mill for a seven-month period were 92.5% of the BOD and 28% of the TOC, and the color increased 7%. Most mills find no color reduction in bio-oxidation and less reduction of TOC than was obtained in the pilot plant. No explanation can be given for these differences in pilot plant and mill results, other than pointing out that the pilot plant bio-oxidation basin received raw effluent, while the mill bio-oxidation basin ponds receive clarified effluent.

Bio-oxidation and incidental air stripping removed 88% of the methanol but none of the acetaldehyde, on the basis of a single set of samples taken during this period of operation. In this set of samples, there were no significant changes in the concentrations of metal ions.

The concentrations of color, TOC, and BOD in the mill effluent as it entered the aeration basin varied widely - as much as four fold from one 24-hr composite sample to another. Such surges were partially dampened by the 6.5-day retention time in the basin, but these surges still caused wide swings in color and TOC concentrations in the bio-treated water fed to the carbon columns, as will be discussed later under carbon column operation.

PRIMARY CLARIFICATION

The basin was used during the period of April, 1972 to December 22, 1972 as an equalization basin and a primary clarifier to provide water to the primary-carbon and the lime-carbon sequences of operation. Mill effluent water was pumped into the basin at a flow rate about 4 gpm greater than was used for the pilot plant, with the excess over-flowing to waste. The aerator was not used. A low degree of mixing in the basin was provided by jetting the incoming water into the basin. Most of the solids in the incoming water settled in the basin, but some further clarification took place in the clarifier section of the basin.

During the period in which the basin was used for equalization and clarification, it was noted that there was anaerobic activity presumably because of the 1-ft to 2-ft layer of sludge (primarily bark fines and fiber) on the bottom of the basin that had accumulated during the bio-oxidation operation. On the basis of 12 analyses, the passage of the water through the equalization basin caused the average methanol concentration to decrease from 45 to 33 mg/l, for a reduction of 27%, and the average acetaldehyde concentration to decrease from 22 to 17 mg/l, for a reduction of 23%, the formic acid concentration to decrease from 10 to 7 mg/l, and the lactic acid concentration to decrease from 1.5 to 0.7 mg/l. The glycolic acid content remained at about 10 mg/l, and the acetic acid content increased from 26 to 92 mg/l, for an increase of 254%. Presumably, this large increase of acetic acid resulted from anaerobic biological growth in the basin. The TOC contributed by these volatiles increased from 48 to 79 mg/l, an increase of 65%. As discussed later, these volatile neutral and acidic compounds contributed substantially to the TOC remaining in the water after carbon adsorption. There was no significant decrease of color, TOC, or BOD on the basis of eight sets of samples, but accurate values of changes in these parameters were difficult to get because of the 5-day time lag of the water going through the basin.

The average amount of suspended solids in the water to the basin was 422 mg/l during the bio-carbon operation but was only 103 mg/l during the lime-carbon operation from September through December, 1972. The amount of suspended solids in the water from the settling basin ranged from 48 to 265 and averaged 145 mg/l. The average turbidity from the settling basin during the primary-carbon and lime-carbon operating periods was 22 JTU.

SECTION VIII

OPERATING RESULTS:

LIME TREATMENT AND CARBONATION

OBJECTIVES AND DESCRIPTION OF OPERATIONS

The lime treatment - carbon adsorption (lime-carbon) sequence was operated from June 30, 1972 to December 22, 1972. A flow rate of 22 gpm was used most of the time and 11 gpm the rest of the time. The lime-treated water was used as feed to the carbon columns at 10 gpm and for FACET carbon adsorption at 10 gpm during most of the period. The lime dosage ranged from 318 to 980 mg/l CaO. This dosage compares with 750-1800 mg/l CaO used or practiced by other pulp and paper companies (5,14,18) as the so-called minimum lime treatment.

Results obtained in the pilot plant in the first few weeks of operation on this treatment sequence, and related results obtained earlier in laboratory inveatigations, had given indications that a color reduction to the 100 CU range by a lime-carbon treatment sequence might be achieved most economically by using a lime dosage substantially below that required to achieve maximum color removal in the lime treatment step. Indications were that the lime dosage might be reduced to the level where the lime-carbon treated water could be reused in the mill without prior removal of soluble calcium by carbonation, thus reducing lime treatment capital and operating costs. This system was dubbed "micro" lime (microlime) treatment, as compared to the "minimum" lime (minilime) treatment in which carbonation for calcium removal is required. The full results obtained in the pilot plant in fact support the microlime - carbon treatment as the treatment of choice to achieve treated effluent quality of 100 CU.

Because of the promising results obtained with microlime treatment followed by carbon adsorption without carbonation of the lime-treated water, most of the data obtained on lime treatment was with low lime dosages of 350 to 700 mg/l of CaO. This microlime period of operation was from July 16, 1972 through December 6, 1972. Carbonation of the microlime treated water was not used because the residual calcium concentration at about 80 mg/l Ca was considered to be low enough for reuse. In December 1972 the minilime treatment process was evaluated at a dosage of about 970 mg/l of CaO. Carbonation of the minilime treated water was used since it would be required in mill operations to recover the soluble calcium and to make the water suitable for reuse in the mill. Carbonation with lime kiln gas removes soluble calcium in one lime treatment installation (14), while natural carbonation accomplishes calcium removal in another (5,18).

In the course of pilot plant operations, it was found that color removal in the carbon colums as well as in lime treatment is directly influenced by the concentration of soluble calcium in the water from the lime treater or to the carbon columns, while lime dosage itself exerts only an indirect influence. However, lack of automatic feed-back control based on soluble calcium dictated continuation of operations based on a predetermined lime dosage. This led to swings in the soluble calcium with changing calcium demand of the effluent based on fluctuations in carbonate ion and color concentration. The control of residual soluble lime in the water from microlime treatment was difficult, not only because of variations in concentrations of carbonate ion and color in the feed water to lime treatment, but also because of long time lags in receiving analytical results on the calcium content of the water. About 40% of the lime added in the microlime treatment was used in converting carbonate ion to $CaCO_3$, but since the carbonate concentration varied as much as 25% in a 24-hr period, the demand for lime for this reaction also varied by 25%. In general, the color in the feed water increased at the same time as the carbonate increased, which caused additional fluctuations in the demand for lime.

Other factors, largely mechanical in nature, in both the lime treater and carbonator caused occasional upsets in the operation. Most of these operating problems were overcome quickly, and changes in equipment or procedure were made to prevent reoccurrence of the same problems.

REMOVAL OF COLOR AND TOC IN LIME TREATER

Data Analysis

As a result of the variations in the composition of the feed water to lime treatment and variations due to mechanical problems, there were few periods for which the effect of independent operating variables could be related to the dependent variables without careful analysis of the data. The dependent variables primarily used in judging performance were color and TOC concentrations of the treated water. The data were analyzed by several means. For a typical day, 30 to 40 items of primary data were logged from operating log sheets and laboratory analysis sheets onto a summary table. These data were also inserted in a computer program which gave a print-out of all primary as well as many secondary calculated values (see Appendix F). Most of the primary items of data were also plotted each day on elapsed-time graphs. These graphs permitted visual correlations of many of the variables. One method of analyzing the data consisted of selecting periods of operation having similar conditions of operation and grouping these into "runs". There were 15 such runs which lasted for periods of 3 to 20 days each.

Another method of data correlation consisted of computer-plotting all values of one property against another property suspected of showing some relationship or of providing more insight to the operation. A third method consisted of obtaining correlation coefficients by computer programs for nine independent versus nine dependent variables and running multiple-regression analyses of these variables. Since many of the dependent variables were largely influenced by the soluble calcium content of the treated water, the data for both lime treatment and carbonation steps were divided into three ranges of calcium concentrations. By this means, this important variable (calcium concentration) could be held essentially constant while the effects of other variables were compared.

Results of Color and TOC Removals in Lime Treater Alone

The results from the treatment of mill effluent with lime in the lime treater without carbonation are given in Table 18. All results, except for days when there were equipment failures and upsets, are averaged under low, medium, and high concentrations of calcium in the product water from the lime treater. The average calcium concentrations in the three ranges were 67, 138, and 228 mg/l. Also, results obtained closer to the preferred microlime level of 80 mg/l have been averaged from the applicable runs in the low and medium calcium range.

As seen in Table 18, the calcium concentration had little relationship to the dosage of lime. This lack of correspondence was caused primarily by variations of Na_2CO_3 (or TIC) and also by variations in color content of the mill effluent to the lime treater. As indicated in Table 18, the total inorganic or carbonate carbon (TIC) of the feed water happened to be high during the low-calcium runs and low during the high-calcium runs. Lime treatment reduced the average color of the feed water 63% when the product water contained 67 mg/l of Ca, 68% with 71 mg/l Ca, 78% with 138 mg/l Ca, and 81% with 228 mg/l Ca. Lime treatment also reduced TOC by 34 to 40% on the average for these ranges of soluble calcium. The BOD content was reduced only 9-13%, which shows that the compounds making up much of the BOD are not very susceptible to removal by lime treatment.

Table 18. AVERAGE RESULTS FROM LIME TREATMENT

	Low calcium		Microlime		Medium calcium		High calcium	
Number of days averaged	36		34		69		16	
Lime dose, as mg/l CaO	478		443		528		576	
as mg/l Ca	342		317		377		412	
	feed	prod.	feed	prod.	feed	prod.	feed	prod.
Calcium (soluble), mg/l	9	67	9	71	15	138	13	228
range, mg/l		17-83		38-103		103-164		172-422
Color, FPCU	1446	1071	1310	977	1670	975	1386	770
CU[a]	712	262	761	243	956	211	842	156
removed, CU %		63		68		78		81
TOC, mg/l	248	163	206	139	275	169	246	146
removed, %		34		33		39		40
TIC, mg/l	64	14	59	12	52	11	34	11
BOD, mg/l	165	151	187	-	261	276	416	348
removed, %		9		-		6[e]		16
pH	9.7	11.8	9.8	11.8	10.1	11.9	10.1	12.0
Conductivity, micromhos	1225	2245	1471	2819	1593	3597	1247	3749
Conductivity increase		1020		1348		2004		2502
Turbidity, JTU	19	53	18	45	24	49	33	72
Volatile organic compounds								
methanol, mg/l	32	34	37	-	36	41	12[b]	14[b]
acetaldehyde, mg/l	30	28	29	-	21	19	3[b]	6[b]
acetic acid, mg/l	115	105	70	-	85	59	46[b]	42[b]
Sludge density, g/ml		1.40		-		1.14		1.27
Sludge, % dry solids		24		-		25		35
Ca tied up by organics, mg/l[c]		117		98		117		120
Atoms of C/atom Ca in organics[d]		2.4		2.3		3.0		2.8

[a] In the product water, filtration preceded adjustment to pH 7.6 in the standard color measurement.
[b] Results from a single sample.
[c] Ca added plus Ca in feed water, minus Ca in product water and Ca in $CaCO_3$ formed with TIC.
[d] Atoms of TOC removed per atom of Ca tied up by organics.
[e] Increase

Influence of Soluble Calcium on Removals

The influence of calcium concentration on percent removal of color in lime treatment and on color remaining is shown in Figure 9. Each point is for a run which consisted of 3 to 20 days during which conditions were fairly constant. The results show that when the average soluble calcium concentration was 80 mg/l, the color was reduced by about 70% and that the calcium content had to be doubled to increase the removal to 80%. The color was reduced to about 230 CU at 80 mg/l Ca and to about 100 CU at about 400 mg/l Ca (which is the calcium content from minilime treatment before carbonation). The TOC data in Table 18 show that removal of TOC in lime treatment was influenced somewhat less than was color removal by the soluble calcium concentration.

The influence of calcium concentration on removals of color and TOC are also discussed in Section XI under results from carbon adsorption following lime treatment. In the lime-carbon sequence it was found that the soluble calcium content had to be at least 60 to 80 mg/l to achieve good removals of color and TOC in the carbon columns.

Spruill (14), in full-scale lime treatment of kraft pulp and paper effluent by Continental Can Co., found a similar influence of calcium content on color removal. The Continental Can Co. uses minilime treatment and a soluble calcium concentration of about 400 mg/l Ca to provide reliable operation and satisfactory removals of color. (In this plant the excess calcium in the water is recovered by carbonation.)

The conductivity of the water was increased by the addition of lime, primarily from the increased NaOH content from the reaction of $Ca(OH)_2$ with Na_2CO_3 but also from the increased concentration of $Ca(OH)_2$. The solubility of $Ca(OH)_2$ (about 1500 mg/l) was not exceeded by the lime dosages used in this program, and therefore essentially all of the lime not used in reaction with organic compounds or Na_2CO_3 went into solution. Any free $Ca(OH)_2$ found in the sludge at these applied lime dosages is a result of insufficient mixing or time for dissolution. The percent increase of conductivity in lime treatment correlated fairly well with the soluble calcium concentration of the treated water, as shown in Figure 10. When lime was added to give a soluble calcium concentration of 80 mg/l, the average conductivity increased from 1600 to 3200 micromhos, for an increase of 1600 micromhos or 100%. The relationship of soluble calcium to conductivity increase might be useful as a rough control of the lime dosage to give a desired concentration of calcium in the lime-treated water.

The turbidity of the feed water ranged from 15 to 35 JTU and that of the lime-treated water averaged about 58 JTU (see Table 18). The turbidity of the product water was largely due to slowly settling floc that was not removed in the clarifier section of the lime treater.

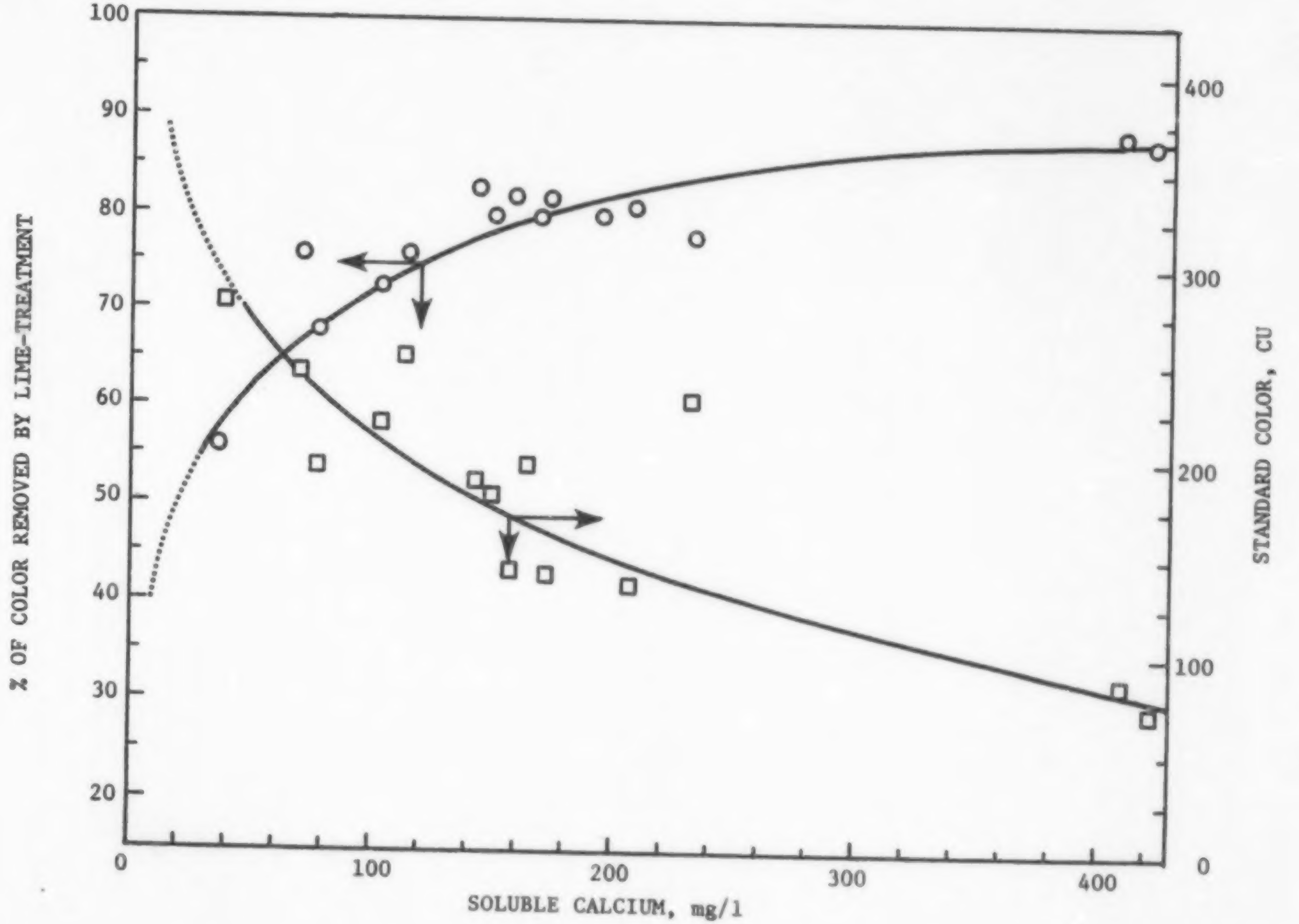


Figure 9. Influence of calcium in lime-treated water on percent of color removed and on color remaining

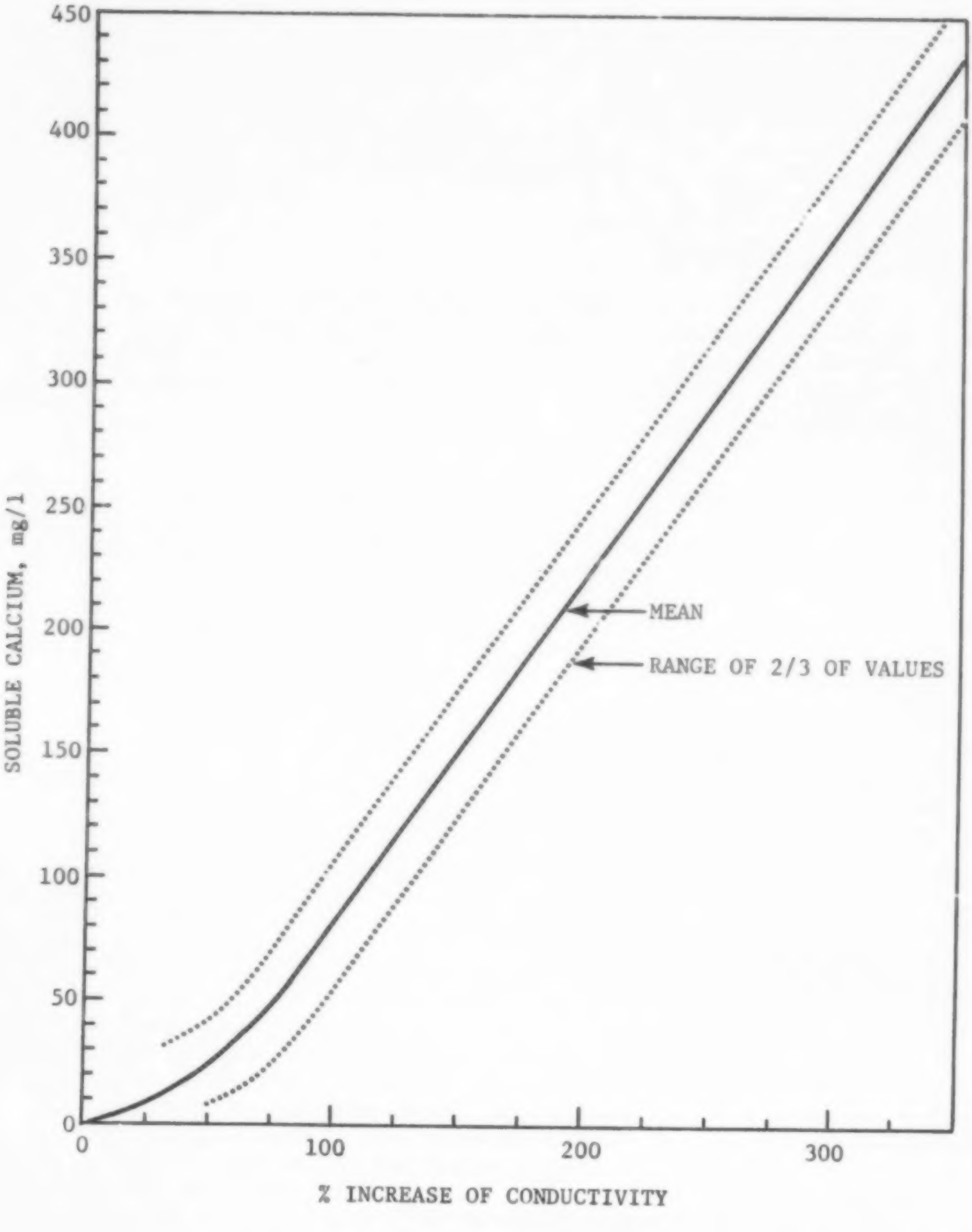


Figure 10. Soluble calcium in lime-treated water versus increased conductivity due to lime treatment

Lime treatment removed very little of the volatile organic compounds, as indicated by the results in Table 18. This result is not surprising since these compounds would not be expected to form insoluble calcium compounds. As discussed in Section VII, it is believed that most of these volatiles were produced by anaerobic activity in the equalization basin. These compounds contributed about 60 out of the 169 mg/l TOC in the product water from the medium-calcium runs.

SLUDGE FROM LIME TREATER

The solids from the lime treater were found to settle rapidly and to form a dense sludge. The average sludge, as withdrawn from the lime treater each morning, contained 28% solids. The solids content of the sludge varied almost linearly with the specific gravity of the sludge as shown in Table 19.

Table 19. RELATION OF SPECIFIC GRAVITY AND SOLIDS CONCENTRATION OF LIME TREATER SLUDGE

Specific gravity, g/ml	Solids in sludge, weight %
1.03	5
1.05	9
1.10	17
1.15	24
1.30	42

The amount of sludge produced per unit of water treated as determined from measurement of sludge volume and solids content was quite variable. Therefore the amount of sludge and sludge solids were calculated from the carbonate removed from the water, the organics removed (TOC), and calcium removed in the sludge with the assumption that no solids were carried out in the treated water. These calculations indicated that during the 69 days of operation with the medium calcium concentration range, the average amount of sludge, expressed as concentration in the product water, was 629 mg/l or 5.2 lb/1000 gal. The sludge solids consisted of about 40% Ca of which 54% existed as $CaCO_3$ (from removal of carbonates), and 46% as calcium-organics. This rather high content of calcium carbonate is evidently the major factor causing the sludge to settle and to filter readily. In contrast, the sludge from minilime treatment of mill effluents is difficult to filter (3,7,8,14) and special precautions are used to add fiber or lime mud from mill operations to make the color-removal sludge filterable. It is also possible that the color compounds which are removed only when the higher lime dosages of the minilime treatment are used are primarily responsible for the poorer settling and filtering characteristics of the sludge from the minilime treatment.

In a filtration test with a representative sample of the sludge from lime treatment, the filtration rate with a vacuum of 24 in. Hg and a final cake thickness of 0.7 in. was 380 lb dry solids per hour per square foot. The cake had a dry solids content of 74%. It appears that the sludge would be suitable for recycle to the lime kiln by adding it to the lime mud before the mill lime mud filters.

The average distribution of calcium in lime treatment is shown in Table 20 for operation at microlime, medium, and high calcium concentrations. The calcium in the product water ranges from a low 71 mg/l (or 22% of the calcium added plus the calcium in the feed water) in the microlime treatment to a high of 228 mg/l (or 54%) in the high soluble calcium treatment. Similarly, the Ca in Ca-organics ranges from 98 to 120 mg/l, increasing with increasing color removal. The Ca in $CaCO_3$ is determined only by the TIC concentration of the feed water since added calcium is consumed in $CaCO_3$ formation before forming Ca-organics and raising the soluble calcium concentration.

It is expected that with good control of lime dosage to give a constant concentration of calcium in the treated water, good lime-carbon operation will be obtained at about 80 mg/l Ca in the treated water and that the loss of calcium to the water will be about 25%.

The amount of calcium in the sludge as Ca-organics was 98-120 mg/l for the four groups of runs (Tables 18 and 20). The average ratio of atoms of carbon in the sludge to atoms of calcium associated with the organics (which is the calcium in the feed plus the calcium added less that in the product water and less that tied up as $CaCO_3$ by the removal of carbonates) was about the same for the four groups of data from lime treatment and ranged from 2.3 to 3.0. The average ratio for all of the lime treatment operation was 2.74 atoms of carbon per atom of calcium. If it is assumed that the organic material removed is "typical" kraft lignin having 9 carbon atoms and 3.3 oxygen atoms per monomeric group, the above average Ca-organic sludge contained 3.3 calcium atoms per monomeric group. The Ca-organics contained, on the average, 0.82 mg TOC/mg Ca, 5.3 CU/mg Ca, and 6.9 CU/mg TOC.

The above Ca-organic atomic composition suggest some difficulty in considering the removal of color from unbleached kraft effluent as a stoichiometric reaction of calcium ions and acidic organic groups such as carboxylic and enolic groups, as Bennett and Dence (52) have shown for kraft bleach effluent. At least a part of the functionality of calcium ions may be explained as coagulation of colloidally suspended substances. No doubt some of the color is originally in colloidal forms, while products of stoichiometric reaction with calcium may form additional colloids.

Table 20. DISTRIBUTION OF CALCIUM IN LIME TREATMENT

	Microlime concentr. of soluble calcium, average of 34 days			Medium concentr. of soluble calcium, average of 69 days			High concentr. of soluble calcium, average of 16 days		
	Feed water mg/1	Prod.water mg/1	Prod.water % of tot.	Feed water mg/1	Prod.water mg/1	Prod.water % of tot.	Feed water mg/1	Prod.water mg/1	Prod.water % of tot.
TIC	59	12		52	11		32	11	
TOC	206	139		275	169		246	146	
Calcium in:									
Ca in feed water	9			15			13		
Ca added as lime	317			377			412		
Ca in, total	326			392			425		
Calcium out:									
Ca in product water		71	22		138	35		228	54
Ca in $CaCO_3$ (from TIC removed)		157	48		137	35		77	18
Ca in Ca-organics (by difference)		98	30		117	30		120	28
Ca out, total		326	100		392	100		425	100

CLARIFICATION IN THE LIME TREATER

The rise rate in the clarification zone of the lime treater was 0.31 gpm/ft^2 or 450 gpd/ft^2 at the normal flow rate of 22 gpm. At this rise rate some of the ca-organic floc failed to settle even though slude from the reaction-mixing zone settled very rapidly. Several modifications were made to provide increased contact between the feed water and the lime to increase the degree of reaction and utilization of the lime. The dosage of lime, in the range we used (including the minilime range) appeared to have little influence on the settling of the small amount of suspended solids in the water.

With the improved conditions of mixing, the average turbidity for the three groups of runs ranged from 19 to 33 JTU in the feed water to the lime treater and from 49-72 JTU in the water from the lime treater. Corresponding values of suspended solids were 170 mg/l in the feed water and 550 mg/l in the water from the lime treater.

Gould (7,8) also encountered flocs that settled slowly in the Georgia Pacific lime treatment of bleach effluent and used synthetic flocculants to remove them.

Carry-over of suspended solids from the lime treater was no problem in the operation of the carbon adsorption columns, although it would be prudent to minimize such carry-over. On the other hand, for direct discharge or reuse of micro-or minilime treated effluent, the level of turbidity and suspended solids observed in this study suggests that means for improved suspended solids removal must be further developed, or provided for in the form of synthetic flocculant, in a commercial installation. One of the changes mentioned above to improve the degree of clarification was to increase the solids concentration in the mixing zone of the lime treater by externally pumping sludge from the bottom of the lime treater to the top of the mixing zone where feed water and lime slurry entered. This modification increased the solids content in the mixing zone from about 4 to 15 g/l. The suspended solids in the water from the lime treater was apparently reduced about 20% by this change.

Another modification was made to improve the degree of mixing and to increase the solution of the particles of $Ca(OH)_2$ by increasing the flow of lime-treated water to the lime slurry mixing tank at the lime feeder. The flow was increased from 2 gpm to 5 gpm which was calculated to be sufficient to dissolve about 40% of the lime from the feeder. Undissolved particles of lime were further dispersed by the centrifugal slurry pump from which a portion of the slurry was recycled to the slurry mixing tank. This increased flow of water to the slurry mixing and the recycling of the slurry through the feed pump caused a markedly visible reduction of white lime particles in the sludge from the lime treater and evidently increased the utilization of the lime.

The turbidity and filterable solids apparently consisted of slow-settling flocculated color bodies. These did not contribute to the measured color and TOC because the water is filtered before these determinations are made. We observed that, if the pH of the samples were reduced to 7.6 before the sample were filtered, the flocculated color dissolved and increased the color of the water after the normal filtration.

OPERATION OF CARBONATOR

Most of the operation of the lime treatment section of the pilot plant was with the microlime process which doesn't require carbonation to remove the excess calcium. When using microlime treatment, the water from the lime treater was allowed to flow through the carbonator as a means of getting the water to the pump that transferred it to FACET carbon adsorption or through the duomedia filter to the carbon columns. The carbonator was used in conjunction with microlime treatment for a period of 11 days to test the effects of low concentrations of calcium (7-23 mg/l) in microlime-treated water on the performance of the carbon columns. Another run was made with the carbonator to provide minilime treatment of water for an 11-day test of carbon adsorption following minilime treatment.

In the minilime run, the lime dosage averaged 920 mg/l CaO with a water flow of 22 gpm. In the lime treater, the color was reduced from 730 to 81 CU for a reduction of 89%, and the TOC was reduced from 212 to 126 mg/l, for a reduction of 40%. The higher lime dosage did not cause noticably improved settling of floc nor reduce the turbidity of the water from the lime treater, as compared to operation at lower lime dosages. Of the calcium going into the system, 63% or 413 mg/l Ca, ended up in the water from the lime treater, compared to 22 to 54% (71 to 228 mg/l) in earlier operations. This concentration of calcium in the water and the degrees of removal agree closely with those obtained by Spruill (14) in full-scale treatment of kraft mill effluent.

The carbonator was operated to reduce the pH to 10.5, the point of least solubility of $CaCO_3$, and to reduce the calcium content from about 400 to 10-20 mg/l. Further reduction of pH to about 8 was obtained with the addition of CO_2 to the pH-adjust tank. Malfunctioning of the pH sensors and CO_2 flow controllers caused occasional increases of calcium in the water from the carbonator above the desired range. The concentrations of color and TOC in the water from the carbonator and pH-adjust tank were normally greater than in the water from the lime treater. This increase was caused by the small amount of floc in the lime-treated water that dissolved at the lower pH of the carbonator and pH-adjust tanks.

The sludge from the carbonator, which is essentially all $CaCO_3$, settled and filtered rapidly and was quite similar to the sludge from the lime treater. In commercial plants, this sludge would be pumped back to the lime treater to be combined with lime treater sludge.

The turbidity of the water from the carbonator was rather high (about 80 JTU). Only a slight reduction of this turbidity was obtained by duomedia filtration. Three potential sources of this turbidity were examined. The first, i.e., floc carry-over from the lime treater, was ruled out because laboratory tests showed that the carried-over lime-color floc redissolves upon carbonation, resulting in an increase in color and in formation of $CaCO_3$. The second potential source of turbidity is carry-over of $CaCO_3$ formed in the carbonator, particularly in the colloidal form. Acidification of samples to pH 6 to dissolve $CaCO_3$ resulted in a turbidity decrease of only about 50%, leaving a white colloidal material in suspension. The nature of this third potential source of turbidity was determined as most likely to be colloidal elemental sulfur formed in the carbonator due to pH reduction of polysulfide-containing effluent, as discussed below.

At times the water from the equalization basin contained as much as 20 mg/l of sodium polysulfide, which caused the lime-carbon treated water to have a bright yellow hue in the absence of carbonation in the carbonator. When effluent samples containing the sodium polysulfide were adjusted to pH 6 or lower, the polysulfide liberated colloidal elemental sulfur which had a white colloidal appearance. Several spot tests indicated significant increases of polysulfide in the water as it passed through the equalization basin. Polysulfide formation probably involves action of anaerobic bacteria on thiosulfate and/or partial oxidation of sulfide to sulfur.

SECTION IX

OPERATING RESULTS:

BIO-CARBON COLUMNS

OBJECTIVES AND DESCRIPTION OF OPERATION

Objectives

The bio-carbon sequence was the first to be operated in the pilot plant. As discussed in Section VII, mill effluent was bio-oxidized and clarified to provide water for the carbon adsorption operation that was typical of the effluent from pulp mills having secondary treatment.

The objectives of the pilot plant operation with the bio-carbon sequence were to determine how successfully carbon adsorption in columns could remove the color and TOC that remained after typical clarification and bio-oxidation of pulp mill effluent and to obtain data needed to design full-scale plants if this method had technical and economic promise. The needed design data included the amount of fresh carbon that is required per 1000 gal of water treated, the contact time (column length and flow rate) of water in the column needed for removals to given levels, pressure drops through the columns, backwash procedures needed, rates of removal of color and TOC, and the effects of anticipated biological activity in the carbon beds.

Clarification and Filtration of Water to Columns

The bio-oxidized water was partially clarified in a section of the basin and then filtered in a duomedia filter to insure that the operation of the carbon columns would not be adversely affected by suspended solids in the water.

A wooden slat fence used to section off a portion of the basin as a damper was only partially effective in eliminating circulation through this section, hence the water discharged was rather high in suspended solids. Toward the end of the bio-carbon sequence, a plastic film covering of the fence resulted in achieving effective clarification in this section.

The duomedia filter contained 12-in layers of anthracite and sand supported on graded gravel. With the normal flow rate of 15 gpm used in the bio-carbon sequence, the flow velocity in the filter was 1.2 gpm/ft^2. By trial and error, we found that mud balls would form in the filter unless it was backwashed twice per week. When it was backwashed, compressed air was used first to help break up any surface accumulation and then water was used for about 10 minutes. The pressure drop just before the filter was backwashed ranged from 10 to 40 psi and averaged 23 psi, but was about 2 psi after backwashing.

The following data, based on 1-5 samples, give an indication of suspended solids levels and turbidity prevailing in this operating sequence:

a. Suspended solids, mg/l: from basin, 190; from filer, 55; from carbon columns, 22.
b. Turbidity, JTU: from basin, 25; from filter, 16; from carbon columns, 12.

Carbon Column Operation

The first carbon column was put on stream on December 17, 1971 and additional columns were added when the water from the columns exceeded about 50 mg/l TOC and 200 CU. After the fourth column had been added and the water from it exceeded the desired levels of color and TOC, the lead column which had been the first column on stream and contained carbon almost fully loaded or spent, was removed from operation on February 3. The spent carbon was discharged and the column was loaded with fresh carbon and put back on line as the last or cleanup column. The columns were designated as Columns A, B, C, and D. Each column was charged with 1600 lb (10 ft bed height) of Atlas Granular Darco 20 x 40 mesh carbon.

The pilot plant was operated from February 4, 1972 to March 11, 1972 with four columns at 15 gpm with a fresh column added whenever the product water TOC exceeded about 60 mg/l. The operation was then continued at 15 gpm until March 18, 1972 with a fresh column added more frequently to test the effect of this higher carbon dosage rate on removal of color and TOC. The flow of water was then stopped and the water in each column was sampled for six days to determine the equilibrium concentrations of the water with prolonged contact time. Average performance data for the lower dosage rate period was based on the period of February 4, 1972 to March 11, 1972 and average performance data for the higher dosage was based on the period of March 11, 1972 to March 18, 1972.

REMOVAL OF COLOR AND TOC BY CARBON ADSORPTION

Plots of color and TOC concentrations of the mill effluent to the bio-oxidation basin, to the columns, and from the columns are given in Figure 11. During the period covered in this figure (February 1, 1972

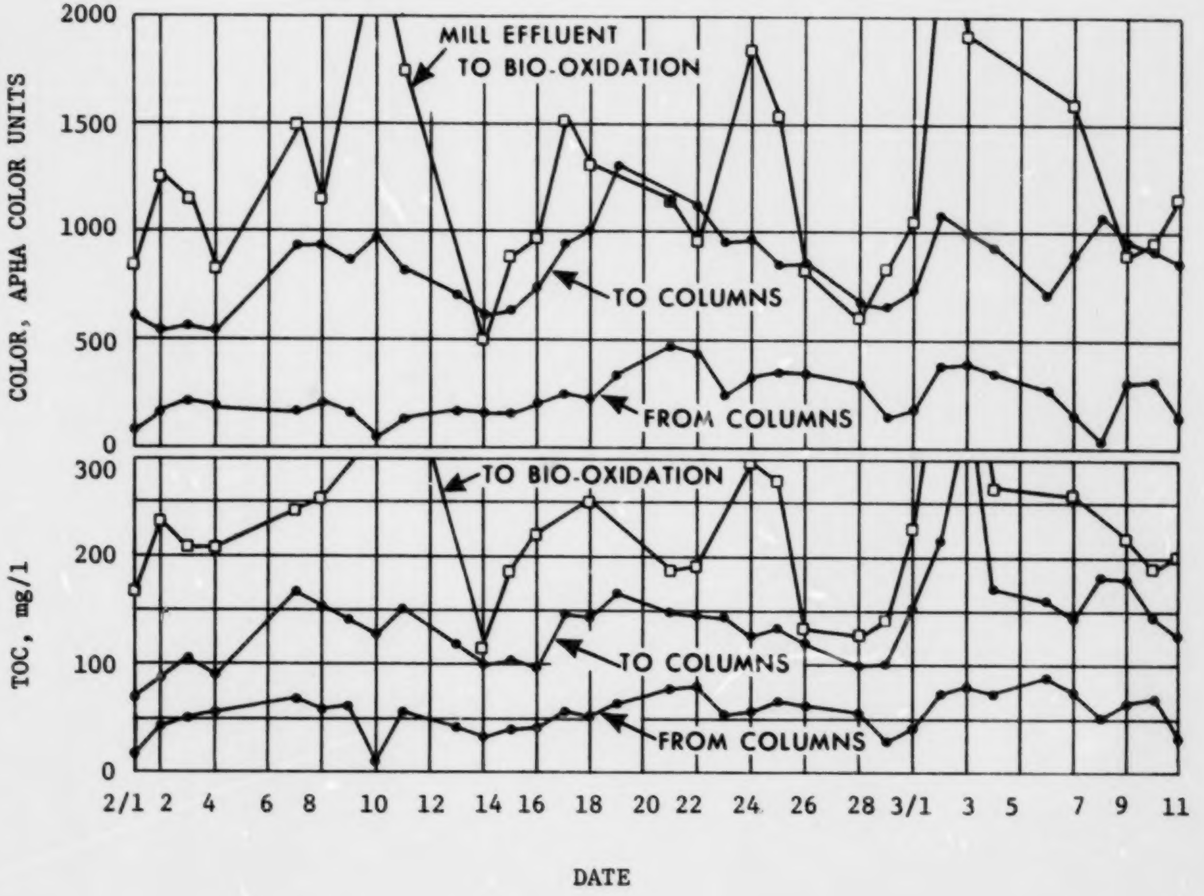


Figure 11. Concentrations of color and TOC during bio-oxidation-carbon adsorption, Feb. 1 through March 11, 1972

to March 11, 1972), the flow was 15 gpm (2.1 gpm/ft^2) through four columns in series. Four fresh columns were added resulting in an average dosage rate of fresh carbon of 8 lb/1000 gal. Note that the concentrations of color and TOC in the 24-hour composite samples of mill effluent to bio-oxidation have a close correspondence, and that both varied widely from day to day.

These wide swings of color and TOC in the water to bio-oxidation were dampened quite a bit by the average retention time of 6.5 days in the equalization basin. The changes of concentration in the feed to the columns usually caused corresponding changes in the product water. The amount of color and TOC removed remained fairly constant in spite of the changes of feed concentration to the columns. The average reductions of color and TOC by carbon adsorption were 578 CU and 91 mg/l TOC.

Average results from the bio-carbon operation for the operating period of February 4, 1972 to March 11, 1972 are given in Table 21. More complete operating results are given in Table 22 for the bio-carbon operation. Included in Table 22 are average results for each of the four column positions and for other measured parameters not included in Table 21. A printout of daily summaries of conditions and results is given in Appendix D.

This mode of operation at a column feed pH of 8.6 and a product pH of 8.2 gave a water with an average concentration of 58 mg/l of TOC, which is expected to be acceptable as a general mill feed water. However, the color level of 230 CU may be too high for some areas in the mill. It is estimated that an additional 25 ft of carbon bed would be required to reach a target of 100 CU in the treated effluent.

This increased length increases the amount of carbon in use (carbon inventory) in the same proportion, i.e., by 63%, while it increases the average dosage rate only by the 25% for the 25% greater amount of color removed. Both factors are important in the economics of the total system. A rather careful determination must be made by each mill, and by the industry as a whole, of actual water quality requirements in terms of color and TOC in reuse water obtained from effluent.

The amount of color and TOC removed in the lead column (Table 22) was greater than in any of the other three columns even though it was fairly well loaded on the average. The amount removed per column became less for each succeeding column. On the other hand, each column removed a nearly equal percentage of its feed.

Table 21. OPERATING SUMMARY OF BIOLOGICAL OXIDATION - CARBON ADSORPTION SEQUENCE AT 15 GPM

LOW CARBON DOSAGE

Number of fresh charges of carbon	4
Average temperature of water to columns ^{o}F	74
Cumulative removal when discharge - CU/g carbon	646
- TOC, mg/g carbon	98
Average dosage rate, lb carbon per 1000 gal water	8
Average retention time of water through 4 columns, hr	2.34
Volumetric flow rate, v/(v hr)	0.43

Color removal	Range	Average
Feed to bio-oxidation, CU	460-2700	1210
Feed to carbon columns, CU	500-1200	810
Product from carbon columns, CU	46- 440	232
Removal by bio-oxidation plus filter, %	-	33
Removal by carbon, % of feed to carbon	-	71
Total removal, % of feed to bio-oxidation	-	81
Rate of removal by carbon, CU/(g hr)	0.40-0.87	0.67

TOC removal		
Feed to bio-oxidation, TOC, mg/l	120- 966	277
Feed to carbon columns, TOC, mg/l	90- 350	149
Product from carbon columns, TOC, mg/l	10- 90	58
Removal by bio-oxidation plus filter, %	-	46
Removal by carbon, % of feed to carbon	-	61
Total removal, % of feed to bio-oxidation	-	79
Rate of removal by carbon, TOC, mg/(g hr)	0.06-0.18	0.11

Table 22. AVERAGE RESULTS FOR BIO-CARBON SEQUENCE FOR PERIOD OF FEBRUARY 4, 1972 to MARCH 11, 1972, LOW CARBON DOSAGE

	General or overall data	Lead column	Second column	Third column	Fourth column
Flow rate, gpm	14.8				
Temperature water to basin, °F	112				
to columns, °F	74				
Color, to basin, FPCU	1610				
CU	1210				
to columns, FPCU	1408				
CU	810				
from columns, FPCU		1170	934	771	666
CU		621	445	319	232
TOC, to basin, mg/l	277				
to columns, mg/l	149				
from columns, mg/l		109	83	70	58
BOD, to basin, mg/l	278				
to columns, mg/l	67				
from columns, mg/l					16
D.O., from basin, mg/l	6.0				
pH	8.6	8.4	8.3	8.2	8.2
Conductivity, micromhos,		1580			1580
Turbidity[b], JTU	16				11
Filterable solids[b], mg/l	55				22
Pressure drop, columns[c], psi		3.6	2.4	2.3	2.3
Color removal rate, CU/(g hr)	0.67	0.87	0.81	0.56	0.40
TOC removal rate, mg/(g hr)	0.11	0.18	0.12	0.06	0.06
Color removed, % to each column		23	28	28	27
Color removed, % to lead column	71	23	22	16	11
TOC removed, % to each column		25	23	16	19
TOC removed, % to lead column	61	24	18	9	9
Color remaining, % to lead column		77	55	39	29
TOC remaining, % to lead column		75	57	49	40
Color removal, CU	578	189	176	126	87
TOC removal, mg/l	91	40	26	13	12
Cumulative color removed, CU/g		603	394	204	78
Cumulative TOC removed, mg/g		87	44	20	8

[a] Four fresh columns were added during this period, so four individual columns served as the lead column, four as the second, etc.

[b] Average of two analyses.

[c] ΔP per column just before backwashing.

The concentration of color and TOC remaining in the water as a function of length of column is shown in Figure 12. This plot can be used to estimate the length of bed required at these operating conditions to reach any desired color or TOC concentration. For example, under these conditions of operation, the length of bed to reduce the color to 100 CU would be about 65 ft, or about 1.63 times that used in the pilot plant (40 ft) which reduced the color to an average of 230 CU. Alternatively, the color could have been reduced to a lower value if the contact time had been increased by reducing the flow rate, but this would have required a much lower flow velocity in the carbon bed, which causes a reduced rate of adsorption (as discussed later in this section) and would also have required a greater amount of carbon per 1000 gal of treated water.

In the case of TOC, Figure 12 shows that the original goal of 50 mg/l could have been reached if the bed length had been increased to 48 ft. These plots show that, with the bio-carbon sequence, the reduction of color to a suitable level is more difficult than the reduction of TOC. This is true only of bio-carbon adsorption because the bio-oxidation in the aeration basin removed less of the color than TOC. In contrast, a greater percentage of color than TOC was removed by the lime treatment step. The concentration of BOD was reduced by 76% by bio-oxidation to 67 mg/l and further reduced 76% to 16 mg/l by the carbon columns, for an overall reduction of 94% by bio-carbon (see Table 22).

The pH decreased from 8.6 to 8.2 as the water passed through the columns. As discussed later, this was perhaps caused by bio-activity in the carbon beds. The average turbidity decreased from 16 JTU in the feed water to the columns to 11 JTU in the water from the columns. The average temperature of the water in the columns was 74°F.

DOSAGE OF CARBON REQUIRED

One of the primary objectives of the pilot plant operation was to determine the amount of fresh carbon or regenerated carbon that is needed per 1000 gal of water to provide water suitable for reuse in the mill. This information cannot be obtained from adsorption isotherms with sufficient reliability. Rather it must be obtained in continuous bench-scale or pilot plant columns and is determined from the average amount of water that can be treated per new column of carbon.

The dosage rate for the test period of February 4, 1972 to March 11, 1972, during which time four fresh columns were added, was 8 lb of carbon per 1000 gal of water, or 940 mg/l. For the period of March 11, 1972 to March 18, 1972 the rate of addition of fresh columns was increased to determine how much the product water quality would be improved by the high dosage rate. On the basis of two column changes, the dosage rate for this period was 26 lb per 1000 gal, or 3.3 times that of the low-dosage period. The results from these two periods are given in Table 23.

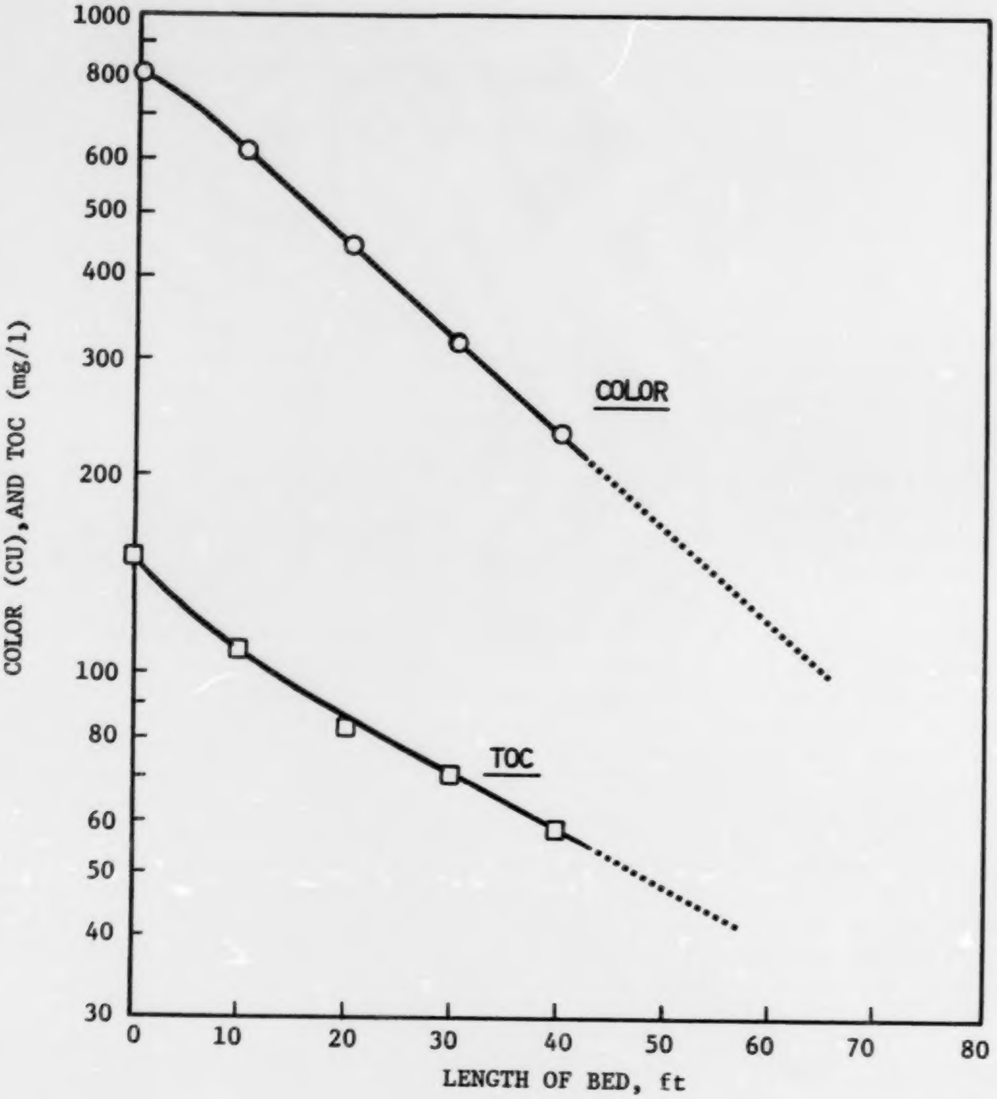


Figure 12. Color and TOC remaining versus length of carbon bed during bio-carbon sequence

Table 23. RESULTS FROM BIO-CARBON ADSORPTION WITH DIFFERING CARBON DOSAGE RATES

	Low carbon dosage rate 2/4 to 3/11/72		High carbon dosage rate 3/11 to 3/18/72	
	Color	TOC	Color	TOC
Conc'n. to aeration basin, CU or mg/l	1210	277	1210	532
to carbon columns, CU or mg/l	810	149	716	161
from carbon columns, CU or mg/l	232	58	226	49
Removal by carbon adsorption, % of feed to columns	71	61	68	70
Rate of removal, CU/(g hr) or mg TOC/(g hr)	0.67	0.11	0.46	0.10
No. of fresh charges of carbon (1600 lb ea.)	4	-	2	-
Cum. removals when discharged, CU/g or mg TOC/g	646	98	327	42
Av. dosage rate, lb carbon per 1000 gal water	8.0	-	26.0	-

Considering, of course, the short duration of the test of high carbon dosage rate, a few points may be noted. Somewhat surprisingly, these results show that the high dosage rate gave only slightly lower concentrations of color and TOC, and a mixed response in terms of percentage removals, rather than the expected strongly increased percentage removals of color and TOC. Because of these unexpected results, it may be speculated that perhaps a dosage rate even somewhat reduced below the 8 lb per 1000 gal of water of the low-dosage period might have achieved nearly equal removals. However, this would not be expected on the basis of equilibrium adsorption isotherms. The average cumulative removal in the first column during operation at 8 lb per 1000 gal was 646 CU/g, which is about 65% of isotherm equilibrium loading and is in line with percentage-of-equilibrium loadings achieved in other carbon column operations.

LOADINGS ON CARBON

The apparent loadings of color or TOC on the carbon are actually cumulative removals per unit weight of carbon. The cumulative removals are greater than the actual loadings of adsorbed impurities because of removals by bio-activity and because a substantial amount of the impurities removed from the water is not actually adsorbed within the pores of the carbon but is apparently held on the outer surfaces of the carbon. Much of this adhering impurity is removed during backwashing, as reported later under a discussion of backwashing.

The cumulative weight of TOC removed by each column per unit of carbon, expressed as mg TOC/g carbon, is shown in Figure 13 as a function of operating time. The cumulative removals of TOC by four columns, by the time they were removed from operation, ranged from 70 to 130 mg/g of carbon during the period of February 4, 1972 to March 11, 1972, and the average removal was 98 mg/g, or 9.8% based on the original weight of carbon (see Tables 22 and 23). The cumulative removals of color for the same period ranged from 495 to 667 CU/g, for an average of 646 CU/g. Average cumulative removals during the period of March 11, 1972 to March 18, 1972, when the carbon dosage was raised to 26 lb/1000 gal, were expectedly lower, i.e., 42 mg/g TOC and 327 CU/g.

RATES OF REMOVAL OF IMPURITIES BY CARBON

The rates of adsorption of impurities on carbon have been studied by a number of investigators. The proposed rate equations based on adsorption of single compounds from solution tend not to fit operating data from complex multi-component systems. The rate of adsorption in weight of a given impurity removed per hour is usually expressed as a direct function of weight of carbon, concentration gradient driving force, temperature of the water, and as an inverse function of carbon particle size. Other factors affecting rate are the pore size and pore size distribution of the carbon, the molecular size and polarity of the material being adsorbed, the degree of turbulence around the particle, and the diffusivity of the impurity in the water. Development of an applicable rate equation for pulp mill effluent is complicated by the countless compounds in the water and the wide variability of the types of compounds. The concentration gradient driving force used in rate equations is the difference in concentration of the water within the pores of the carbon, or its equilibrium adsorption concentrations, and the concentration of the bulk solution. Again, the development of an applicable rate equation is complicated by the fact that the equilibrium concentration within the carbon is not known. The equilibrium concentration could be determined from an equilibrium adsorption isotherm for the same water and carbon if one knew the loading on the carbon. But the indicated loading or cumulative removal of the impurity per unit weight of carbon that is measured is not the same as the true loading, as discussed above.

Because of these complicating factors, we used a simplified rate expression which is the amount removed per weight of carbon per hour, or CU/(g hr) and mg TOC/(g hr). The rates were calculated (by the computer program) each day for each column from the amounts of impurity removed and the weight of carbon in each column. These rates are of value in comparing the effects of operating variables on rates and for designing full-scale plants. The rates are directly applicable only to water of the same composition and temperature, the same type and size of carbon, the same velocity and retention time of the water in the columns, and the same rate of addition of fresh carbon (dosage rate).

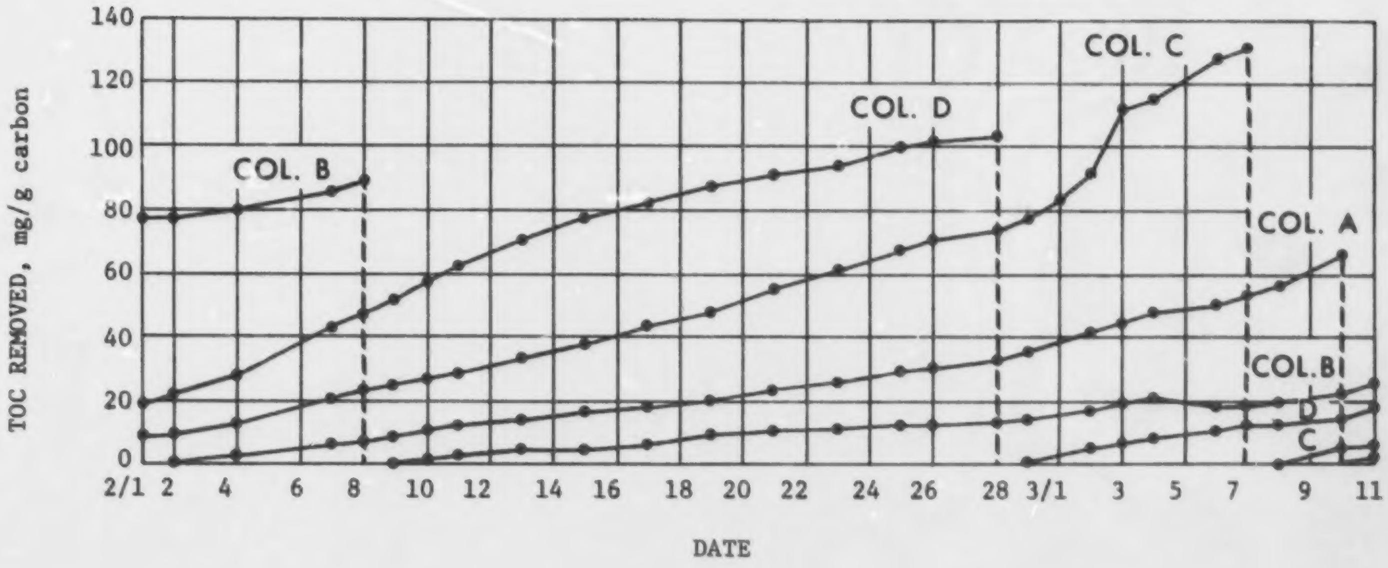


Figure 13. Cumulative removals of TOC on carbon, Feb. 1 to March 11, 1972

The rates of removal in the pilot plant columns during the bio-carbon sequence were highest in the lead column, in which the concentrations were highest, and were lowest in the last column in which the concentrations were lowest (see Table 22). During the period from February 4, 1972 to March 11, 1972, the average rates of removal by column position ranged from 0.87 CU/(g hr) for the first column to 0.40 CU/(g hr) for the fourth column, and the overall average rate was 0.67 CU/(g hr) (see Table 22). The corresponding rates of removal of TOC were 0.18 and 0.06 mg/(g hr), with an average of 0.11 mg/(g hr). These results are shown graphically in Figure 14 as a function of bed length. Note that the highest rates were observed with the lead column that had the most fully loaded carbon and contained the highest concentrations of impurities in the water. The rates of adsorption in a given column as it was moved through the four column positions are also indicated by the slopes of the cumulative removal curves of Figure 13.

The rates of removal are plotted versus average concentration in each column in Figure 15. These curves show that rates are very dependent on bulk solution concentration. The effect of concentration would be much greater if the depressing effect of loading on the carbon had not been present.

The equations for rates of removal of color and TOC for the curves given in Figure 15 are:

$$\text{Color removal rate} = 0.523 \ln C - 2.55, \text{ for } 250 \text{ to } 800 \text{ CU}$$
$$\text{TOC removal rate} = 0.194 \ln C - 0.77, \text{ for } 70 \text{ to } 150 \text{ mg/l TOC}$$

Where rate is in CU/(g hr) or mg TOC/(g hr), C is average concentration in CU or mg/l.

As stated above, backwashing of the columns removed some of the color and TOC that had been loosely held by the carbon. There was no evidence that the rate of adsorption was increased by a higher frequency of backwashing, even though this would be expected.

The rates of removal were less when the high dosage rate of carbon was used (March 11, 1972 to March 18, 1972), even though the cumulative removals, or degree of loading of the carbon, were only 50% of those during the low dosage period (February 4, 1972 to March 11, 1972) (see Table 23). It is postulated as one possible explanation, that the external coating of organic matter on the carbon, as discussed earlier, was an overwhelming rate-controlling mechanism, which nullified the effect of fresher carbon from the high-dosage operation. However, the short duration of operations at high dosage rates makes this comparison less than definitive.

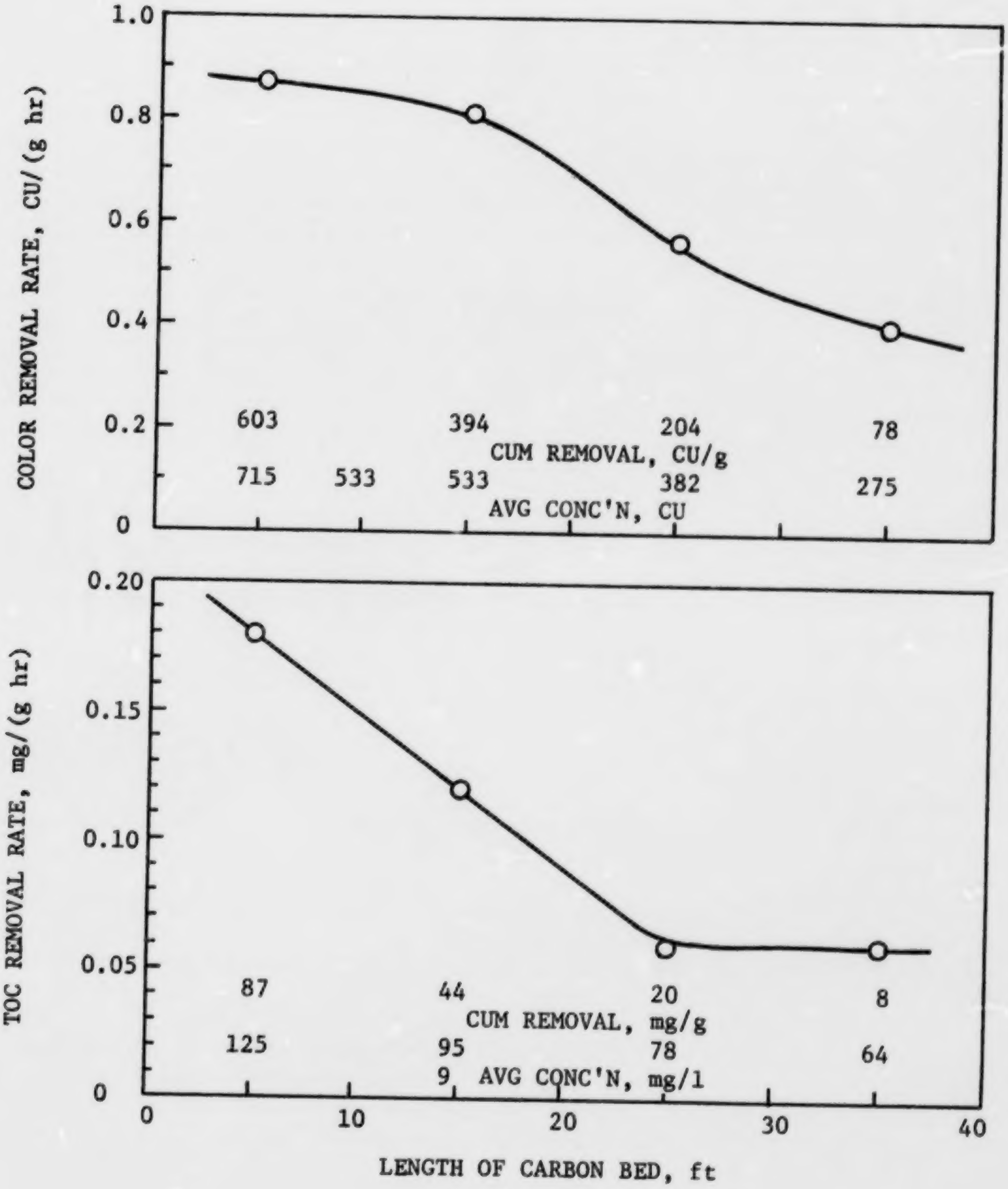


Figure 14. Rates of removal of color and TOC by carbon adsorption during bio-carbon sequence, Feb. 4 to March 11, 1972

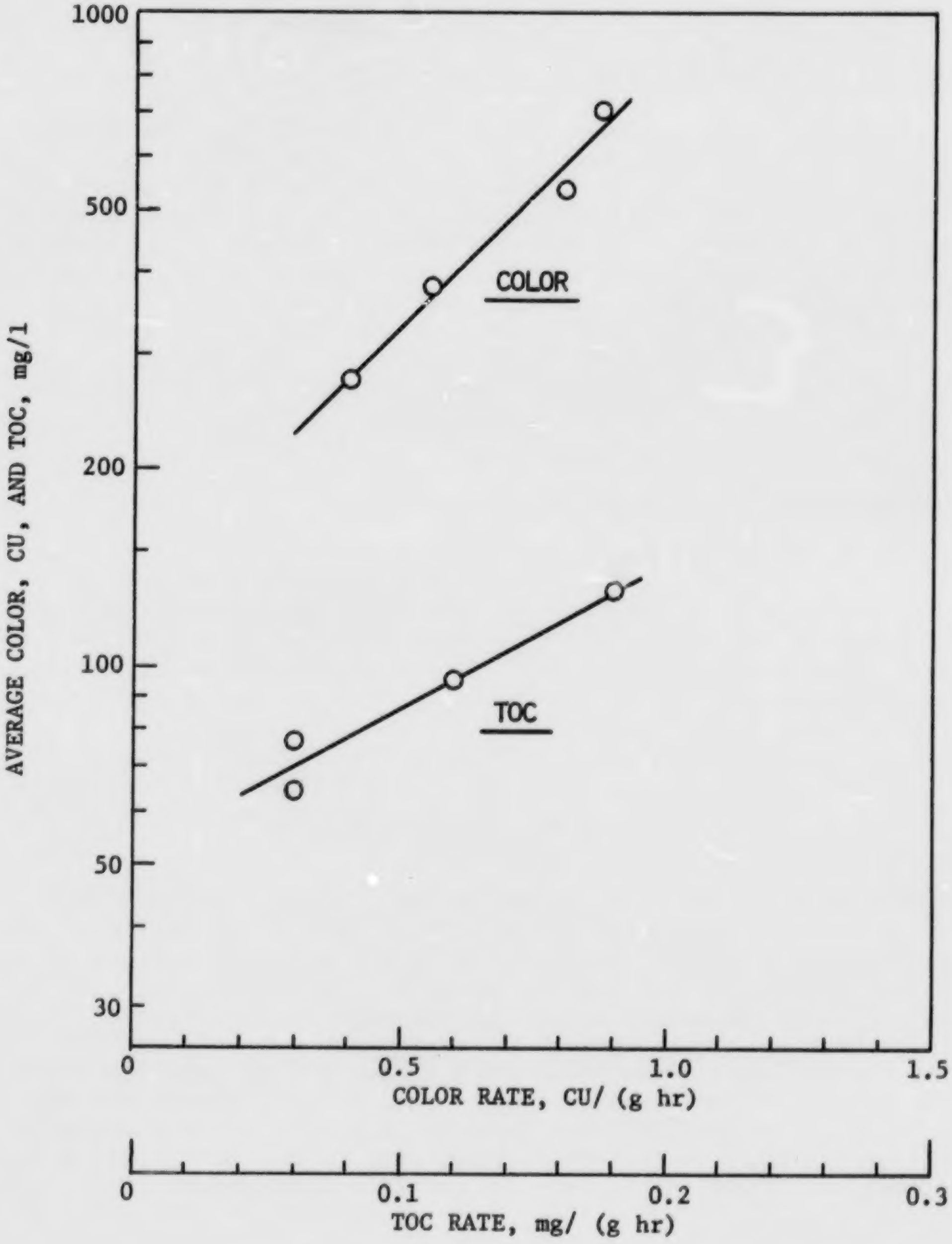


Figure 15. Rates of removal of color and TOC by carbon columns as a function of average concentration during bio-carbon operations, Feb. 4 to March 11, 1972

EFFECT OF FLOW VELOCITY ON RATES OF ADSORPTION

The superficial (empty-column) velocity of water through the columns at 15 gpm was 2.1 gpm/ft^2. A lower velocity would give a longer contact time in the four columns for a greater reduction of color, but it was not known whether the lower velocity would cause lower rates of removal per unit of carbon due to an increase in the thickness of the stagnant layer of water around each carbon particle. Special runs were made at 0.7 and 1.75 gpm/ft^2 which indicated that at the higher velocity of 1.75 gpm/ft^2 the rate was only slightly higher than at 0.7 gpm/ft^2. The results of these tests are discussed more fully later in conjunction with tests made during the primary-carbon sequence of operation (see Section X).

BIOLOGICAL ACTIVITY IN CARBON COLUMNS

There was evidence of some aerobic and anaerobic bio-activity in the carbon columns, as is more fully discussed under the primary-carbon sequence in Section X. The average dissolved oxygen content of the feed to the columns during the bio-carbon sequence was 6 mg/l but decreased rapidly to less than 1 mg/l in the water from the first column. However, very little removal of TOC (about 3 mg/l) can be attributed to biological consumption of the 6 mg/l of dissolved oxygen based on stoichiometric considerations. Most of the aerobic activity appeared to be concentrated in the top one or two feet of the first column, evidenced by caking of carbon particles and column plugging unless the columns were backwashed every one or two days.

Anaerobic activity was also present in the columns, as indicated by bacterial analyses made near the end of the bio-carbon operation. The total bacterial count was low in the mill effluent to the basin and very high from the basin. The concentration was reduced from 3.6×10^6 to 2.1×10^6/ml by the sand filter. The concentration was further reduced to 1×10^6/ml in passage through the carbon columns. All but about 0.1% of the bacteria were retained on a 0.8 micron filter. Hydrogen sulfide producing bacteria were present in the feed to the columns, but the water from the columns had very low concentrations of these bacteria. Occasionally, there was evidence of H_2S odor in the water from the columns. Anaerobes were found in the water to and from the columns.

BACKWASHING OF CARBON COLUMNS

The columns were backwashed by a high rate of flow of compressed air for about 20 sec followed by an up-flow of 30 gpm of well water for a period of 20 minutes every other day. The backwash water was black and contained about 10% of the color and TOC that had been removed by the columns during the two days of adsorption. When the columns were backwashed at the two-day frequency, the average pressure drop through the four columns in series was about 10 psi before backwashing and about 3 psi after backwashing.

CORRELATION OF VARIABLES

The interactions of 12 independent variables with 18 dependent variables during the bio-carbon operation of February 4, 1972 to March 11, 1972 at 15 gpm were examined by a computer regression analysis. The results of this analysis generally confirmed the conclusions from the direct analysis of the data. The 12 independent variables included temperature, pH, and concentrations of color and TOC to the columns, and cumulative removals of color and TOC from each of the four columns. (The term cumulative removal is used in preference to loading for reasons stated earlier in this section.) The 18 dependent variables included color and TOC concentrations from each column, removal rates of color and TOC for each column, and percentage removals of color and TOC from the collective columns.

This regression analysis of the data showed that the color of the water from the fourth column was largely a direct function of the color to the columns, the cumulative removals of color and TOC by the first two columns, and the cumulative removal of TOC of the fourth column, i.e., the product color increased as the feed color increased and as the cumulative removals increased. The color from the other columns was primarily a function of the color in the feed to the first column. The percentage removal of color by the four columns was almost entirely explained by the cumulative removals of color by the four columns, i.e., the percentage removal decreased as the cumulative removals increased.

The TOC in the water from the fourth column was primarily a direct function of the cumulative removals of TOC by the first and fourth columns and of the TOC concentrations of the feed water to the first column.

The rates of removal of color by the columns were influenced as an inverse function of the cumulative removals by the columns. The rate of removal of TOC by the group of four columns was strongly influenced (directly) by the TOC concentration of the feed water and to a lesser degree by the color of the feed water, and was weakly influenced (inversely) by the cumulative removal of color by the first column.

The variation in temperature during this period of operation was not very great: 66% of the values fell between 81 and 67°F, with the average being 74°F. In this range, temperature had no significant influence on adsorption performance.

SECTION X

OPERATING RESULTS:

PRIMARY - CARBON COLUMNS

OBJECTIVES AND DESCRIPTION OF OPERATION

Objectives

The objectives of the primary-carbon operation were to determine whether carbon adsorption without pretreatments by bio-oxidation or lime treatment could remove the much larger amounts of color and TOC at high enough loadings on the carbon to give reasonable values of carbon dosage (regeneration rates) and sufficiently low capital and operating costs to make this sequence competitive with the other two sequences. Preliminary economic estimates (see Section V) had indicated that the primary-carbon sequence might be competitive with the lime-carbon sequence. Since the concentrations of color and TOC would be high, the rates of adsorption and the loadings on the carbon were expected to be considerably greater than with the other sequences. Other objectives were to determine the flow velocities and contact times needed for removal of impurities and to determine whether this sequence of operation would give unique problems, such as excessive bio-activity within the columns and greater rates of pressure-drop increase.

Operating Periods

The primary-carbon sequence was in operation from April through the first week in September, 1972. Four columns were operated in series in downflow, eight weeks at 10 gpm, and four weeks at 5 gpm. Carbon columns were replaced regularly throughout these periods. Two columns were operated in series for the subsequent 11-week period in downflow at 10 gpm without any further carbon changes to observe the long-term capacity of the system for removing color and TOC.

PRIMARY CLARIFICATION AND FILTRATION

The basin was used for primary clarification and for equalization of impurity concentrations in the mill effluent before it was fed to the carbon columns. Water was pumped into the basin at a rate of 15 gpm which gave a retention time of about 8 days. As pointed out in Section VII on Primary Clarification and Bio-Oxidation, anaerobic activity in the basin caused an increase of low-molecular-weight compounds that are not absorbed by activated carbon. The average TOC content of these compounds was 48 mg/l in the water to the basin and 79 mg/l in the water from the basin, for an increase of 65%.

Even though the equalization basin provided a retention time of 8 days, the feed to the columns varied from 1550 to 540 CU and 410 to 170 mg/l TOC during the period covered by these results. The rates of change of concentrations in the feed to the columns were generally less than 100 CU per day and 20 mg/l TOC per day. These fluctuations in feed concentration introduce a high degree of complexity into the correlation of operating results with operating conditions.

In a commercial installation for treating effluent by lime treatment or carbon adsorption, or both, effluent concentrations to the treatment system must be held in a narrower range, and rapid changes in effluent concentrations must be avoided through in-plant control measures or external spill basins and equalization basins. The suspended solids in the water to the basin varied widely - from 37 to 790 mg/l. The water after primary clarification contained from 50 to 265 mg/l and averaged 168 mg/l of TSS. The turbidity of the water from primary clarification ranged from 18 to 23 JTU.

The water to the columns was not sand-filtered prior to the carbon columns except during the first three weeks. Insufficient data were obtained to determine the amount of suspended solids removed by the duomedia filter when it was being used. The pressure drop across the columns before each backwash remained the same as when the water was filtered. Therefore, we concluded that filtration ahead of the columns is not required if the effluent to the columns contains less than about 200 mg/l suspended solids and the columns are backwashed on a schedule as discussed later in this section. This suspended solids level may well be achievable, depending on the mill, by grit and floating solids (bark) removal alone or by clarification in a relatively small clarifier at high overflow rate.

REMOVALS OF COLOR AND TOC BY CARBON ADSORPTION

The results from carbon adsorption following primary clarification (primary-carbon) are summarized in Table 24 for two periods operating at two different flow rates (10 and 5 gpm). Detailed data for each of the four columns are given in Table 25 for the operating period at the higher flow rate (10 gpm). A printout of daily summaries of conditions and results is given in Appendix E.

The product water during the 10-gpm run contained, on the average, 185 CU and 83 mg/l of TOC. These values are somewhat greater than may be desired for reuse in the mill. The relationship of product concentrations to

Table 24. SUMMARY OF PRIMARY CLARIFICATION - CARBON ADSORPTION SEQUENCE

Dates	4/25-5/20	5/20-6/22
Flow rate, gpm	10	5
Flow rate, gpm/ft^2	1.42	0.71
Flow rate, vol water/vol carbon/hr	0.28	0.14
Contact time, hr	3.5	1.8
Number of fresh charges of carbon	4	3
Cummulative removal when discharged		
CU/g carbon	350	360
TOC, mg/g carbon	61	70
Average dosage rate, lb carbon per 1000 gal	20.5	28
Color removal		
Feed to carbon columns, CU	791	997
Product from carbon columns, CU	185	202
Removal by carbon, %	77	80
Rate of removal by carbon, CU/(g hr)	0.69	0.46
TOC removal		
Feed to carbon, TOC, mg/l	220	310
Product from carbon, TOC, mg/l	83	121
Removal by carbon, %	62	61
Rate of removal by carbon, mg/(g hr)	0.11	0.08

Table 25. AVERAGE RESULTS FOR PRIMARY-CARBON SEQUENCE FOR PERIOD OF APRIL 4, 1972 TO MAY 20, 1972 AT FLOW RATE OF 10 GPM

	General data	Lead column	Second column	Third column	Fourth column
Temp. water to basin, ^{o}F	114				
to columns, ^{o}F	76				
Color, to columns, FPCU	1474				
CU	791				
from columns, FPCU		815	588	483	368
CU		483	322	259	185
TOC, to columns, mg/l	220				
from columns, mg/l		126	110	99	83
pH from columns		10.0	10.0	9.9	9.4
Cond., micromhos		876	850	840	830
Turbidity, JTU		20	18	17	17
Susp. solids, mg/l, from basin	168				
from cols.					85
Pressure drop, psi		1.0	1.0	1.0	1.0
Color removal rate, CU/(g hr)	av. 0.69	1.66	0.60	0.24	0.27
TOC removal rate, mg/(g hr)	av. 0.11	0.30	0.05	0.03	0.05
Color removal, % to ea. col.		39	33	20	29
Color removal, % to lead col.	tot. 77	39	20	8	9
TOC removal, % to ea. col.		43	12	9	17
TOC removal, % to lead col.	tot. 62	43	7	5	8
Color remaining, % to lead col.		61	41	33	23
TOC remaining, % to lead col.		57	50	45	38
Color removal, difference, CU	tot. 606	308	161	63	74
TOC removal, difference, mg/l	tot. 137	94	16	11	16
Cumulative color removal, CU/g		270	101	48	21
Cumulative TOC removal, mg/g		45	16	9	5

length of column is given in Figure 16. By extrapolation, the length of column needed to reach 100 CU at 10 gpm and under the same other conditions of operation would be about 60 ft, or about 50% more than was used in the pilot plant runs.

It is assumed in this extrapolation that the compounds that would be removed at the lower concentrations would have the same adsorption properties as those already adsorbed. This assumption may not hold for the low-molecular-weight compounds that make up a portion of the TOC. To reach a color of 100 CU, the inventory of carbon would have to be increased by 50% and the carbon dosage rate would have to be increased by about 14% for the increased amount of color removed.

The lead column removed a large portion of the total color and TOC removed by the four columns. As shown in Table 25 during the 10-gpm run, the lead column removed 39% of the feed color, the second column removed 20%, the third removed 8%, and the fourth removed 9%. The lead column removed 51% of the total color removed by all columns and 70% of the total TOC removed. The possible mechanisms accounting for this large percentage removal in the first column are given later in a discussion of the ultimate removal capacity and mechanisms in carbon columns.

In contrast to the above large removals in the first column during primary-carbon operation, the first of the four columns in the bio-carbon operation removed only 33% of the total color that was removed and 40% of the TOC. The lower removals in the lead column in the bio-carbon sequence might be due to the organic compounds being less bio-degradable after the bio-oxidation treatment and that bio-activity was greater in the primary-carbon columns. The removal of BOD was not determined for the primary-carbon sequence of operation.

DOSAGE OF CARBON REQUIRED

The most reliable way to determine the carbon dosage rate with fixed-bed columns is to continue a pilot plant operation until the number of fresh columns added are two greater than the number of columns in series, e.g., six for the primary-carbon operation. The dosage rate is then found by dividing the weight of carbon in each column by the average volume of water treated between column changes. In this primary-carbon run at 10 gpm, we added fresh columns six times and discarded the data from the first two column changes because these columns had been used during the bio-carbon sequence and thus the data would not be typical of results from the primary-carbon sequence. The time interval between the next four column changes ranged from 92 to 160 hr and averaged 130 hr. Therefore, the dosage rate was:

$$\frac{\text{1600 lb carbon per column change} \times 1000}{130 \text{ hr} \times 600 \text{ gal/hr}} = \frac{20.5 \text{ lb}}{1000 \text{ gal}}$$

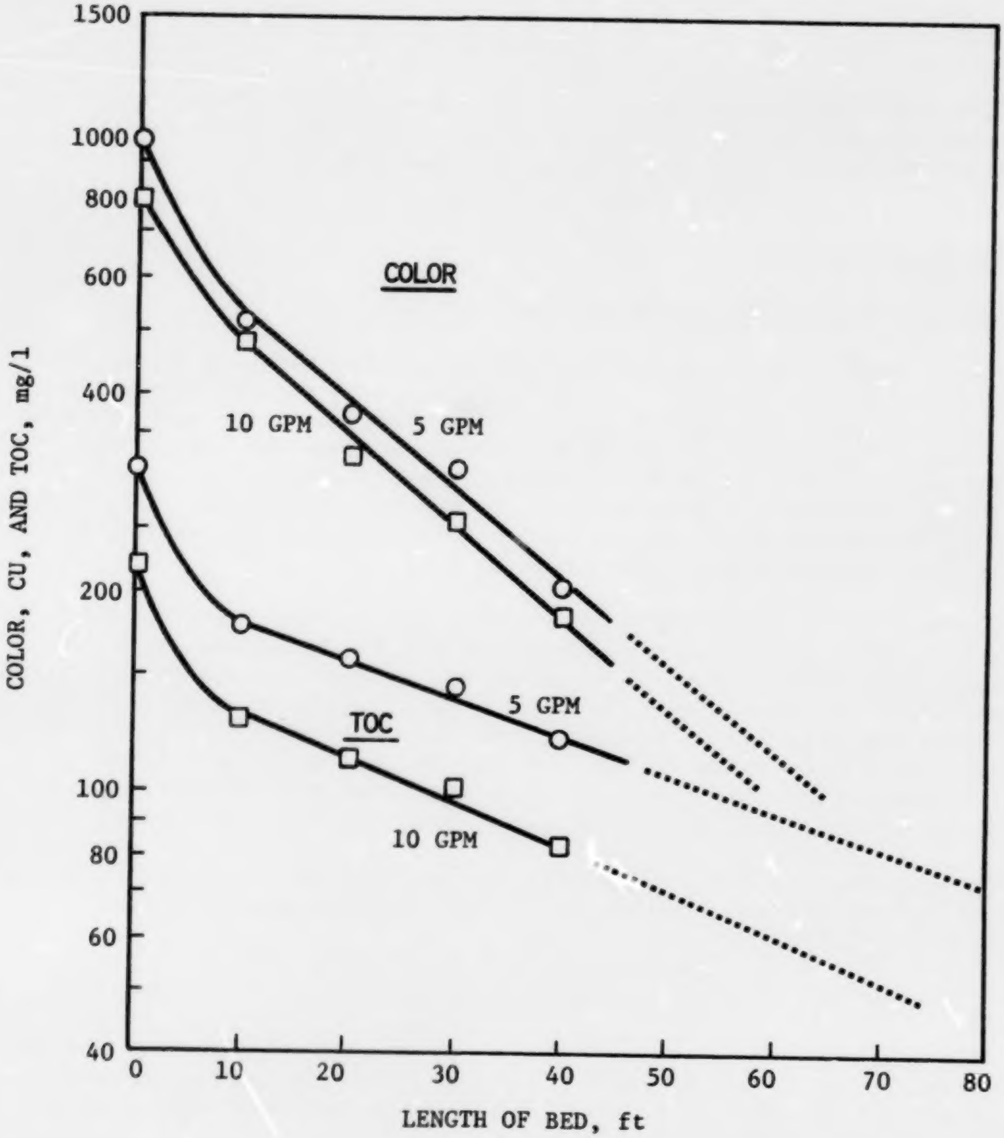


Figure 16. Color and TOC remaining versus length of bed during primary-carbon sequence

During the 5 gpm run, five columns were added and the average time between changes for the last three columns added was 251 hr and the average dosage rate was 28 lb carbon per 1000 gal.

RATES OF ADSORPTION

Adsorption Rates During 10 gpm Run

The average rates of removal by each column for the 10 gpm run, April 25, 1972 to May 20, 1972, are given in Table 25 and are plotted in Figure 17 as a function of average concentration of the water in each column. The rates during the bio-carbon sequence are also shown. The rates of removal of color and TOC appear to be linear with the log of concentration over most of the concentration range. A discussion of factors affecting adsorption rates is given in Section IX on the bio-carbon sequence of operation.

In the case of the primary-carbon data, the average rates for the third column were lower than those for the fourth column which is surprising because the fourth column had a lower average concentration. The rates of removal by primary-carbon were lower than those of the bio-carbon sequence at concentrations below 130 mg TOC/l and 330 CU but were higher at the higher concentrations. The higher rates in the lead column of the primary-carbon sequence were evidently caused by non-adsorptive phenomena discussed later in this section.

The equation for the relationship between the rate of removal of color and the concentration during the 10-gpm run with primary-carbon sequence is as follows:

$$\text{Rate, CU/(g hr)} = 1.83 \ln C - 10.2$$

where C = average color concentration in the columns, CU

This equation is only approximate and is strictly applicable only for a color range of 300 to 700 CU, for water with the same properties as was used in the pilot plant, and for the same other operating conditions used in the pilot plant run.

The equation for TOC removal rates, which is limited to the TOC range of 100-200 mg/l and to the conditions used in the pilot plant run is:

$$\text{Rate, mg TOC/(g hr)} = 0.55 \ln C - 2.5$$

where C = average TOC concentration in the columns, mg/l

Effect of Velocity on Adsorption Rates

The effect of velocity on adsorption rates was investigated during the bio-carbon and the primary-carbon sequences of operation. The EPA

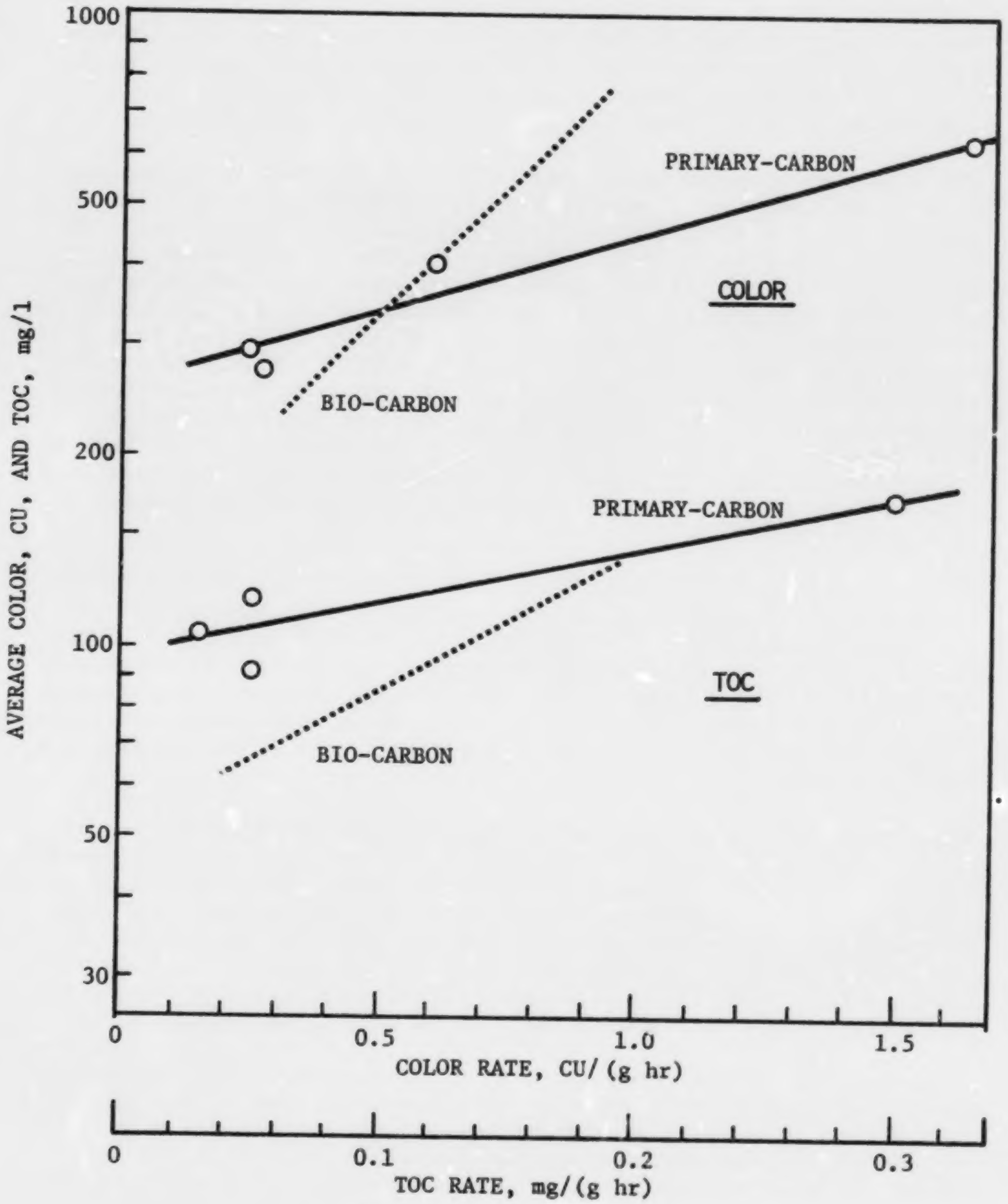


Figure 17. Rate of removal of color and TOC by carbon adsorption during primary-carbon operation at 10 gpm

Process Design Manual for Carbon Adsorption (19) stated that several studies have found that velocity in the range of 2-10 gpm/ft^2 is not a limiting factor in fixed-bed granular carbon adsorption. Other investigators (9,17) found no effect in the 4-10 gpm/ft^2 range.

The effect of velocity was studied at the end of the bio-carbon operation. The last two columns were used, one with a flow of 5 gpm (0.7 gpm/ft^2) and the other with a flow of 12 gpm (1.75 gpm/ft^2) with the same water being fed to both. Samples of treated water were removed at different lengths of the carbon beds to give equal retention times of water in the columns. After four days of operation, the conditions were reversed so that the previous high-velocity column was then the low-velocity column. This switching of conditions should remove the effect of the degree of loading in each column from the comparison. Results showed that the percentage removals and rates of removals were the same for color removal and about 10% greater for TOC removal in the case of the high velocity run. Therefore, this test indicated that an increase of velocity from 0.7 to 1.75 gpm/ft^2 was beneficial by a slight amount.

The influence of velocity was also studied during the primary-carbon operation by comparing results from periods of operation at 10 gpm (1.4 gpm/ft^2) and 5 gpm (0.7 gpm/ft^2), as reported in Table 24. The feed during the 5 gpm run was unfortunately 25% greater in color and 40% greater in TOC concentration. The average product concentrations were also greater for the 5 gpm run, even though the percentage removals of color (77 and 80%) and of TOC (61 and 62%) were about the same for the two periods.

Since rates of removal are highly dependent on the concentration of the impurity in the water in the adsorption beds, the rates of removal at the two velocities were compared at the same concentrations on a plot of rate versus average concentration in each column. The rates of removal of color obtained at 10 gpm for April 25, 1972 to May 20, 1972 were two times those at 5 gpm when they are adjusted to the same water concentration. The rates of removal of TOC at 10 gpm were more than three times those at 5 gpm at the same water concentrations.

These results indicate that rates of adsorption were substantially greater at a superficial velocity of 1.4 gpm/ft^2 than at 0.7 gpm/ft^2. This effect of velocity in the primary-carbon sequence was much more pronounced than was observed in the bio-carbon sequence discussed above. We conclude that commercial plants should use a velocity of at least 1.4 gpm/ft^2 and perhaps as much as 2-4 gpm/ft^2 subject to limitation by the cost of pumping.

The pumping energy requirement and pressure drop through the columns increase in direct proportion to the lineal velocity of flow. To maintain the same color removal, the length of column needed will also by increased in direct proportion to the velocity cut will be decreased by the greater adsorption rate afforded by the greater velocity. The net effect of increased velocity on energy requirements will lie between velocity to the first power and velocity squared.

The pumping energy required at 4 gpm/ft^2 to remove color from 1000 to 100 CU was estimated to be only about $0.004/kgal and the total pressure drop was estimated to be about 40 psi.

CORRELATION OF VARIABLES

The interactions of 12 independent variables with 18 dependent variables during the primary-carbon operation of April 25, 1972 to May 20, 1972 at 10 gpm were examined by a computer regression analysis. The results of this analysis generally confirmed the conclusions from the direct analysis of the data. The 12 independent variables included temperature, pH, and concentrations of color and TOC to the columns; and cumulative removals of color and TOC from each of the four columns. The 18 dependent variables included color and TOC concentrations from each column, removal rates of color and TOC for each column, and percentage removals of color and TOC from the collective columns.

This regression analysis of the data showed that the percentage removal of color by the four columns was almost entirely explained by the (inverse) effect of cumulative removals of the columns. The cumulative removal of the first column had the greatest influence, primarily because this column removed more of the total color than the other columns.

The TOC removal rates were only weakly influenced by the various conditions (lineal velocity was constant during this operating period). The rate was influenced by color and TOC concentrations of the feed (higher concentrations caused higher rates) and to a lesser extent by the cumulative removals of the carbon (higher cumulative removals caused lower rates).

The overall color removal rates were primarily a (direct) function of color concentration in the feed. In the second and third columns the rate was still largely dependent on feed color concentration but was also directly related to cumulative removals. Therefore in these two columns, the rate increased as the cumulative removals increased, for unknown reasons. In the first and fourth columns, the rate decreased as the cumulative removals increased as would be expected. The rate in the fourth column was primarily due to the cumulative removals of color and TOC of the first column as well as that of the fourth column.

The concentration of TOC from the fourth column was primarily a (direct) function of cumulative removals of color and TOC by the first and fourth columns and secondarily a (direct) function of the color and TOC concentrations in the feed.

The color from the fourth column was primarily a (direct) function of the color of the feed and of the cumulative removals of TOC and color by the second and third columns.

PRESSURE DROPS AND BACKWASHING OF COLUMNS

During essentially all of the primary-carbon runs, from April 4, 1972 to June 22, 1972, the four columns were backwashed every other day, and the water fed to the columns from the equalization basin was not filtered after the first month of operation. During the period of June 22, 1972 to July 8, 1972, backwashing was discontinued to determine how rapidly the pressure drop across the columns would increase and to determine whether a reduced frequency of backwashing could be used. The flow rate during this 9-day test period was 10 gpm through the four columns in series. There was no substantial increase of pressure drop across the four columns; the final pressure drop was only 3 psi. The columns were all backwashed and two columns were then operated at a flow of 10 gpm and were backwashed once per week. After two weeks of operation, the pressure drop increased to 8 psi across the two columns and to 44 psi after four weeks. An inspection of the tops of the beds showed that the top two feet of both carbon beds had become almost solid with particulates removed from the water and with biological growth. The hard layer was broken up with hand tools and with vigorous backwashing. The run was then continued but with a backwashing frequency of once every two days. The pressure drop per column just before backwashing varied from 1 to 30 psi, but averaged about 4 psi.

The amount of lost production caused by backwashing amounts to 20 minutes each time or 10 minutes per day, when backwashing every other day, or only 0.7% of the normal daily production. The volume of backwash water for 15 minutes of backwashing at three times the normal flow rate would amount to 23 minutes of production per day, or 1.6% of the daily production. However, it is expected that the water from backwashing would be reused for backwashing after being settled or treated by coagulation to remove most of the material displaced during backwashing. The volume of water needed to be held for backwashing could be further reduced by backwashing several columns in series.

DISPLACEMENT OF TOC AND COLOR FROM COLUMNS DURING BACKWASHING

The water coming from the columns during backwashing was very black and contained a substantial amount of color and TOC. Tests were run to determine the quantities of color and TOC that were displaced during backwashing of the columns. Four of the tests were during the primary-carbon runs and one during the bio-carbon runs. In these tests the flow of water from the column being backwashed was held constant at 30 gpm and samples of the backwash water were taken about five times during a backwash period of 20-60 minutes.

In one of the tests that was continued for 60 minutes, it was estimated that a total backwashing time of 110 minutes would be required before the backwash water would no longer contain an appreciable amount of color or TOC and that approximately half of the total displaceable materials were displaced in the normal backwash period of 20 to 30 minutes. The backwash from the lead column did not contain much greater concentrations of color and TOC than that from the second or third columns. The average results from these five tests given in Table 26 show that backwashing displaced about 11% of the color and TOC that had been removed by the carbon since the prior backwashing.

The ratio of filter paper color (FPCU) to Millipore color (MPCU) is a measure of the size of the colloids that make up a portion of the color. During the period of maximum color displacement by backwashing, the ratio of FPCU/MPCU was 3.7 but decreased to 1.7 for the average backwash water. The amount of color in the size fraction less than filter paper and greater than 0.8 micron Millipore size was 274% of that in the "true" color range of minus 0.8 micron Millipore filter. During the average backwashing period this percentage decreased to 65%. These results indicate that the color bodies displaced during the first part of the backwashing period are much larger in size than those displaced later in the period and that a large portion of the apparent color (FPCU) is not "true" color (MPCU). The color bodies in the more highly colored initial fraction of backwash water contained 18 FPCU per mg of TOC; whereas the average backwash water contained 9 FPCU per mg of TOC. The feed water to the columns during the primary-carbon operation contained only about 5 FPCU per mg of TOC. This comparison of FPCU/TOC ratios indicates that the color bodies that are deposited during normal operation and displaced during backwashing are not only much larger than the color bodies in the feed water but are much more intense in color per atom of carbon they contain.

Table 26. DISPLACEMENT OF COLOR AND TOC DURING BACKWASHING OF COLUMNS

	Color		TOC,	Ratio	
	FPCU[b]	MPCU[c]	mg/1	FPCU/MPCU	FPCU/TOC
Average[a] max. concentration	3674	983	210	3.7	17.5
Average concentration	1213	734	137	1.7	8.9
Amt. displaced per g carbon	8.3	3.6	0.56		
Hrs. of loading removed in backwashing		4.1	9.4		
Amt. displaced in backwashing as % of amt. removed in normal operation since last backwash		11	11		

[a] Average of results from backwashing of 8 columns in 5 tests for 20 to 60 minutes each.

[b] Measured after filtration through Whatman No. 2 paper filter.

[c] Measured after filtration through 0.8 micron Millipore filter.

NON-ADSORPTIVE REMOVAL MECHANISMS IN CARBON COLUMNS

The objective of the third operating period of the primary-carbon sequence was to determine the residual removal capacity of the two most spent columns without further carbon replacement. A potentially significant residual removal capacity of the carbon had been inferred during preceding operations when significant removals were still being obtained from the first or lead column (which is the most nearly spent column) just prior to its replacement as necessitated to maintain desired quality of effluent from the fourth column. This prolonged test of residual removal capacity was continued 15 times the normal length of time between column changes, with backwashing.

This run was carried out with the third and fourth columns from the previous primary-carbon runs using primary clarified water from the basin at a flow of 10 gpm to the columns. The columns were backwashed every two days. During this run, no fresh carbon was added. The run was continued for a total of 74 days from June 26, 1972 to September 9, 1972 until the rates of removal appeared to have reached a constant value. After the first 23 days, the color removal rates for both columns had decreased significantly and were about 0.5 CU/(g hr), but the TOC rates had decreased only to about 0.15 mg/(g hr). During the following 21 days, TOC removal rates continued to drop, while color removal remained essentially steady. During the final 30 days of the run, both color and TOC removal were fairly constant and were about the same for the second column as for the first column. The average final equilibrium removal rates were 0.5 CU/(g hr) and 0.06 mg TOC/(g hr). As shown in Table 27 these rates were 20-30% of those in the first column during the primary-carbon run of April 25, 1972 to May 20, 1972, also at 10 gpm.

Table 27. COMPARISON OF REMOVAL RATES OF EXHAUSTED CARBON WITH NORMAL OPERATION

	Removal Rates	
	Color, CU/(g hr)	TOC, mg/(g hr)
Final exhaustion run[a] 8/9 to 9/9/72, 10 gpm	0.5	0.06
Adsorption run[b] 4/25 to 5/20/72, 10 gpm	1.66	0.30
Exhaustion run rate as percent of adsorption run rate	30%	20%

[a] For both columns
[b] First two columns

During the final 30 days of this run, fairly wide fluctuations in concentrations of the water to the columns had very little effect on removal rates, compared to a strong dependence during normal operation. Also, removal in both columns proceeded at equal rates, although water concentrations decreased from the first to the second column. In normal operation, removal rates in the second column are substantially below those in the first column, as seen in Table 25. By the beginning of the final 30 day period, cumulative removals had increased to levels well beyond equilibrium loadings estimated from a number of isotherms on similar effluent (see Section XIII, Figures 26 and 27). Cumulative removals actually amounted to the following multiples of equilibrium loadings: color, first column, 3.5, second column 3.5; TOC, first column, 1.7, second column, 1.8. Allowing for partial displacement during backwash as discussed earlier in this section would reduce these factors by a maxiumum of 20%.

These data and observations suggest that during this extended run, adsorptive TOC removal had essentially ceased by the beginning of the final 30-day period, while adsorptive color removal had ceased prior to that time. Continued removal of both color and TOC therefore requires explanation by other mechanisms. These mechanisms are probably also operative during normal operation. Potential mechanisms include biological activity, filtration, and colloid destabilization.

Evidence of bio-activity was found in samples of carbon from the columns containing high concentrations of organisms similar to those found during bio-carbon operation discussed in Section IX. Biological mechanisms are generally believed not to effect color removal from kraft effluent. On the other hand, removal of COD and TOC by bio-activity in carbon columns has been found to amount to an appreciable portion of total COD and TOC removals in work with municipal effluents (6,16,37). The dissolved oxygen in the column feed water during the primary-carbon operation, including the extended run discussed here, was always less than 1 mg/l, hence any bio-activity must have been anaerobic, after consumption of the restricted amount of oxygen in the top one to two feet of the first column. The reported rates of TOC digestion in anaerobic sludge digestors for a large number of installations were equivalent to 0.01 to 0.02 mg/(g hr) when adjusted to the volumes of solids and the temperatures in the carbon columns. Therefore, anaerobic activity could account for 0.01 to 0.02 mg TOC/(g hr) out of a removal rate of 0.06 mg TOC/(g hr) during the final period, that is 17 to 33% of the total TOC removal.

Filtration undoubtedly occurs in the carbon columns (the sand-filter was not in use during the extended run), as evidenced by the reduction in suspended solids (see Table 25). However, it must be borne in mind that TOC is measured on a paper-filtered (about 2 micron) basis, while color is measured on a Millipore-filtered (0.8 micron) basis. Hence, any explanation of color removal by filtration in the column implies the removal of particles less than 0.8 microns in size, which are extremely difficult to filter, or less than 2 microns in the case of TOC.

A mechanism of colloid destabilization and coagulation in conjunction with filtration is suggested to explain the unexpected removals of color and TOC. This mechanism is further discussed in Section XIII. Destabilization may occur due to removal of stabilizing substances by adsorption or bio-activity, or by a more direct functionality of the carbon surface. The destabilized colloidal particles coagulate and are then more readily trapped by the carbon in the column by a filtration mechanism. Such filtered substances would then be subject to displacement from the column by backwashing. The displacement by backwashing amounts to about 20% of the color and TOC removed from solution between backwashes during normal operation. During the extended operating phase (final 30 day period), this amount is equivalent to displacing by backwashing 66% of the color and 100% of the total TOC removed from solution between backwashes. During the latter period, the backwash water did contain substantial amounts of black suspended materials, however, no quantitative data on these were obtained.

Undoubtedly, a number of different mechanisms are at work simultaneously. Similarly, during normal operation removals are probably increased above strictly adsorptive removal by the non-adsorptive mechanisms in evidence during the extended run. It may be argued that during normal operation the rates of non-adsorptive removal are as high as those shown above, i.e., that 20% of the TOC removal normally observed is non-adsorptive, consisting perhaps of up to 7% by bio-activity and 13% by the suggested colloid destabilization - filtration mechanism. At the same time, 30% of the color removal is non-adsorptive and is removed by the colloid destabilization - filtration mechanism if bio-activity may be held (as is generally done) not to affect color.

SECTION XI

OPERATING RESULTS:

LIME - CARBON COLUMNS

OBJECTIVES AND DESCRIPTION OF OPERATION

The sequence of lime treatment followed by carbon adsorption (lime-carbon) was evaluated while treating mill effluent that was passed through the equalization basin and lime treatment at a flow of 22 gpm. The operation of lime treatment was described in Section VIII. The lime-treated water was fed to two carbon columns in series at a flow of 10 gpm, or 1.4 gpm/ft^2. The total height of carbon bed was 20 ft, which provided a superficial contact time of 1.8 hr and a bed volume rate of 0.55 volume of water per volume of carbon per hour. The columns were backwashed every two days.

The major objective of this lime-carbon sequence of operation was to determine the operating performance of the carbon columns with mill effluent treated by the microlime process, as discussed in Section VIII. The goal of the microlime treatment was to use dosages of lime sufficiently low to provide treated water with such low dissolved calcium content that there would be no need for carbonation. This level of dissolved calcium was defined as about 80 mg/l Ca, or a range of 60-100 mg/l. On the other hand, the microlime treatment was expected to be sufficient to make any remaining color and TOC readily removable by carbon column adsorption.

REMOVALS OF COLOR AND TOC; EFFECT OF SOLUBLE CALCIUM CONCENTRATION

The microlime-carbon treatment was shown to be capable of reducing color to less than 100 CU and TOC to about 100 mg/l, when the level of soluble calcium was in the 50-100 mg/l range. The percentage removals of color and TOC by carbon adsorption increased and the concentrations of color and TOC in both the feed and product water from the columns decreased as the soluble calcium concentration of the water from lime treatment to the carbon columns increased. Removals of color and TOC appeared to be independent of pH in the range of 7 to 12.

Final color and TOC levels obtained in the combined lime-carbon treatment are shown in Figure 18 as a function of dissolved Ca in the column feed. Each point represents a run consisting of consecutive daily results within a fairly narrow range of dissolved calcium. Runs immediately after column changes are identified as squares in this figure (three runs).

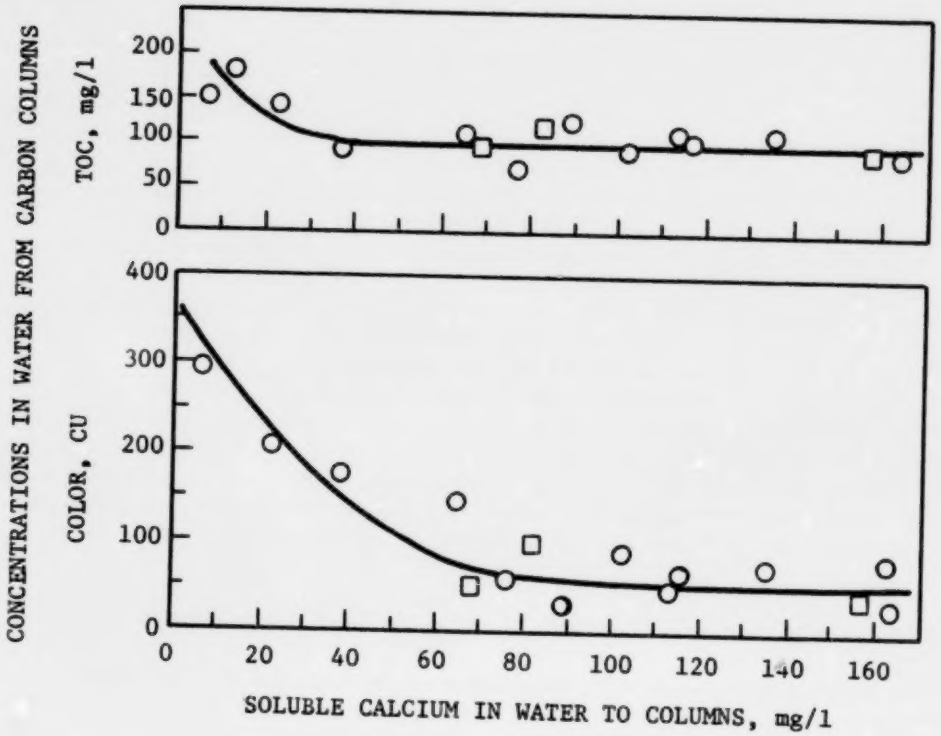


Figure 18. Effect of calcium concentration on removal of color and TOC by carbon adsorption (averages from operating periods)

The data in this figure include all runs regardless of whether or not carbonation was used after lime treatment, using for correlation in all cases the dissolved calcium in the column feed. As this figure shows, both color and TOC tend to level off when more than a certain dissolved calcium concentration is maintained, i.e., the color was about 60 CU at calcium concentrations above 80 mg/l, and TOC was about 100 mg/l with calcium concentrations above 40 mg/l. Other factors such as service age of the carbon and concentrations of the feed to the lime treater caused some fluctuations from the levels stated.

Since the soluble calcium content of the water to the columns (and the related concentrations of color and TOC) was found to have a major influence on the adsorption of color and TOC from the water, data from all of the lime-carbon operation were grouped into ranges of soluble calcium in the water to the columns. The operating conditions and results of the lime-carbon operation are given by this method of grouping in Tables 28 and 29. Additional results from the carbon adsorption step are given in Table 30. A printout of daily summaries and conditions is given in Appendix G.

In the low-calcium range of 10-50 mg/l, which averaged 42 mg/l, carbon adsorption reduced the color from 276 to 214 CU, or by only 22%. At the medium-calcium range of 50-100 mg/l, which averaged 86 mg/l, good removals of color were obtained in the carbon columns, with the feed color reduced from 252 to 76 CU. This removal was 71% of the color to the columns (Table 30) and was 21% of the color to the lime treater. The total removal by the lime-carbon sequence in the medium lime range was 91%.

Color measured after filtration through 2-micron paper filters was found to give valuable insight into the colloidal nature and size of the color bodies. A comparison of colors of product water after being filtered through filter paper and through 0.8 micron Millipore filters shows that a large portion of the apparent (unfiltered) color of the treated water at low calcium levels was caused by colloidal color bodies or colloidal calcium carbonate smaller than about 2 microns and larger than 0.8 micron.

TOC removal was influenced less than color removal by the calcium concentration, probably because a larger portion of the TOC is made up of compounds that do not react with calcium. With the medium-calcium runs, the TOC was reduced to 100 mg/l TOC to give a reduction of 44% of the TOC in the feed to the columns and 28% of the feed to lime treatment. The total removal of TOC in lime-carbon treatment was 63%.

The variation of color and TOC concentrations of water with length of carbon adsorption bed are shown in Figure 19 for the three groups of runs. The slope of these lines is steeper as length of column increases, thus, in contrast to the results with the primary-carbon runs, the last (second)

Table 28. LIME-CARBON SEQUENCE OF TREATMENT:

REMOVALS OF COLOR AND TOC

	Low calcium	Med. calcium	High calcium
Soluble Ca to cols., mg/l range	10-50	50-100	100-200
avg.	42	86	138
Lime dosage, $Ca(OH)_2$, mg/l	592	692	709
CaO, mg/l	448	523	536
pH of water to columns	9.7	11.3	11.6
Color CU			
to lime treatment,	861	852	937
to carbon columns	276	252	200
from carbon columns	214	76	61
TOC, filtered, mg/l			
to lime treatment	225	272	275
to carbon columns	165	177	165
from carbon columns	118	100	98
% removal of color to lime trt.			
in lime treatment	68	70	79
in carbon columns	7	21	15
total	75	91	94
% removal of color to columns	22	70	70
% removal of TOC to lime trt.			
in lime treatment	27	35	40
in carbon columns	21	28	24
total	48	63	64
% removal of TOC to columns	29	44	41

Table 29. SUMMARY OF CARBON ADSORPTION FOLLOWING LIME TREATMENT:

REMOVALS OF BOD AND TURBIDITY

	Low calcium	Med. calcium	High calcium
Soluble Ca to cols., mg/l range	10-50	50-100	100-200
avg.	42	86	138
Lime dosage, $Ca(OH)_2$, mg/l	592	692	709
pH of water to columns	9.7	11.3	11.6
BOD, mg/l			
to lime treatment	234	166	254
to carbon columns	212	150	235
from carbon columns	128	130	171
% removal of BOD to lime trt.			
in lime treatment	9	10	8
in carbon columns	36	12	25
total	45	22	33
Turbidity, JTU			
to lime treatment	26	24	24
to carbon columns	52	30	50
from carbon columns	30	12	7

Table 30. CARBON ADSORPTION TREATMENT OF LIME-TREATED EFFLUENT

FLOW = 10 GPM

	Low calcium		Med. calcium		High calcium	
No. of days averaged	21		30		64	
Soluble Ca to cols., mg/l range	10-50		50-100		100-200	
avg.	42		56		138	
Temperature from cols. °F	81		86		81	
Hours since fresh col., 1st col.	1390		1056		1103	
2nd col.	796		447		396	
pH	9.7		11.3		11.6	
	To	From	To	From	To	From
Color, FPCU, 1st col.	1000	897	1092	724	914	455
2nd col.		649		254		188
CU, 1st col.	276	253	252	180	200	145
2nd col.		214		76		61
TOC, mg/l, 1st col.	165	139	177	144	165	133
2nd col.		118		100		98
BOD, mg/l	212	128	150	130	235	171
Turbidity, JTU	52	30	30	12	50	7
Conductivity, micromhos	2245		3597		3749	
% removals in columns	1st	2nd	1st	2nd	1st	2nd
Color, % of color to 1st col.	8	14	29	41	28	42
total		22		70		70
TOC, % of TOC to 1st col.	16	13	19	25	20	21
total		29		44		41
BOD removal, total, %[a]		40		13		27
Rates of removal						
Color, CU/g hr	0.18	0.30	0.41	0.66	0.40	0.44
avg.	0.25		0.54		0.42	
TOC, mg/g hr	0.08	0.07	0.10	0.14	0.10	0.11
avg.	0.075		0.12		0.11	

[a] Some values are averages of only 2 or 3 determinations

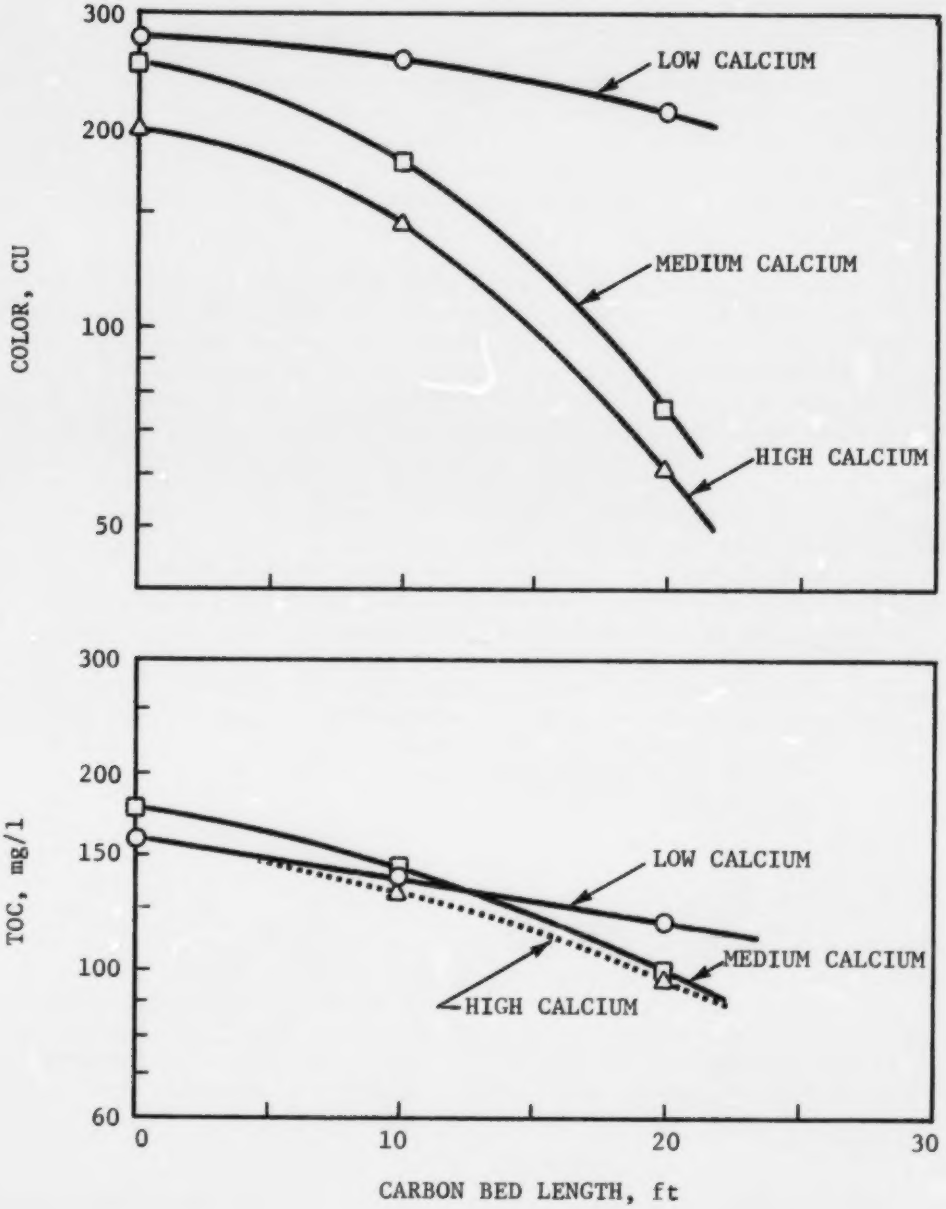


Figure 19. Concentrations of color and TOC remaining versus length of carbon bed

column in lime-carbon adsorption had a greater adsorption rate than the lead column, especially in the case of color adsorption. These curves show that with the medium level of soluble calcium and with the other operating conditions used in the pilot plant, the length of bed needed to reach 100 CU is 17 ft and the length needed to reach 100 mg/l TOC is 20 ft.

The color remaining in the water from each column as a function of operting time is given in Figure 20. The color is expressed as a percentage of the feed color to each column to normalize to some extent the variation of feed concentration. A similar plot of data for TOC concentrations is given in Figure 21. These curves show that there is an immediate breakthrough of nearly 50% of the TOC, and a rapid breakthrough of some of the color as well, in the second column after it is added as the fresh column. In the case of TOC, the water from the fresh column jumped within one day to 40-50 mg/l TOC, which was caused by the non-adsorbable low-molecular-weight compounds in the water.

The color and TOC concentrations after each step in the lime-carbon sequence are shown in Figure 22 for the medium-calcium runs. Note that the color drops sharply in lime treatment as compared to a smaller percentage drop in TOC concentration. The slight increase of color and TOC in the carbonator-filter step was caused by the use of carbonation during one run of this four-run medium-calcium group. As discussed previously, carbonation caused redissolution of floc not removed in the lime-treater clarifier.

DOSAGE OF CARBON REQUIRED

The lime-carbon sequence was operated for a relatively long time primarily to provide reliable information on how much water could be treated by carbon adsorption per unit weight of fresh carbon. Since the lime-treated feed water to the columns had low concentrations of color, it was necessary to operate an average of 44 days before the product water increased in color and TOC to the point that a fresh column was needed. The lime-carbon sequence was operated for a total of 160 days, and four fresh columns of carbon were added.

On the basis of the last three column changes, the average dosage of fresh carbon used was 2.5 lb per 1000 gal. The dosage requirements would be lower if the total bed length were increased, the contact time increased, or the feed water contained less color and TOC.

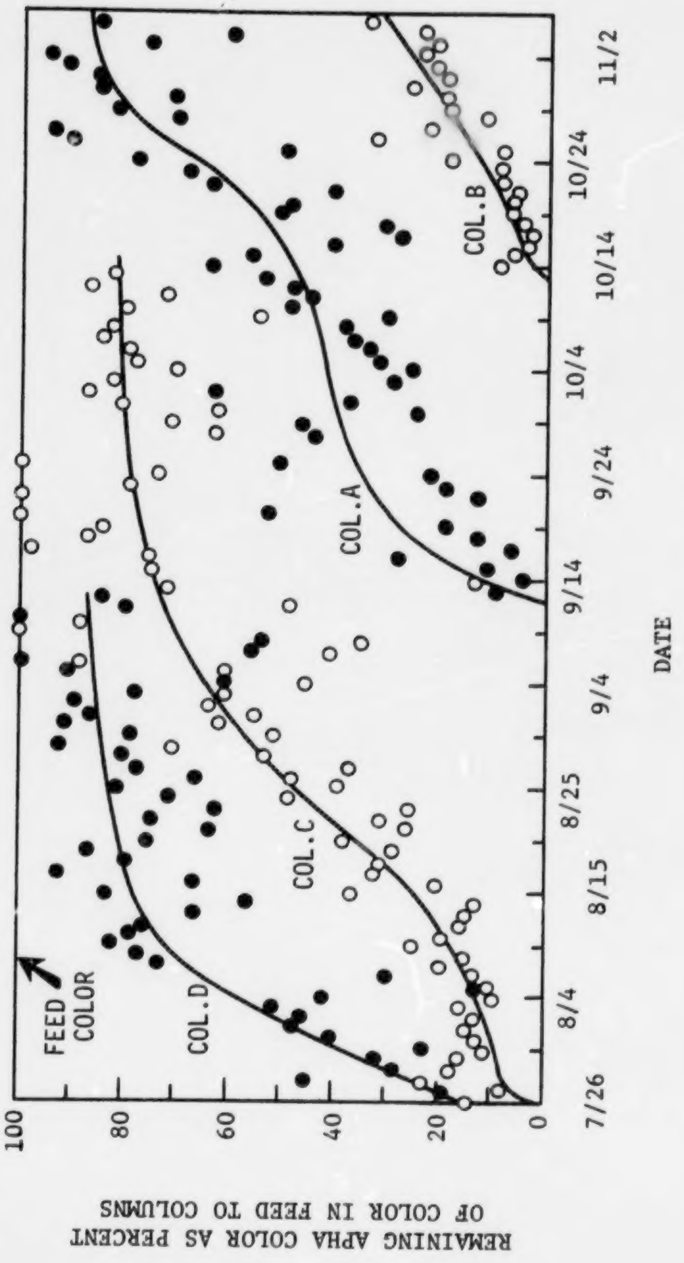


Figure 20. Remaining color in water from columns during lime-carbon sequence

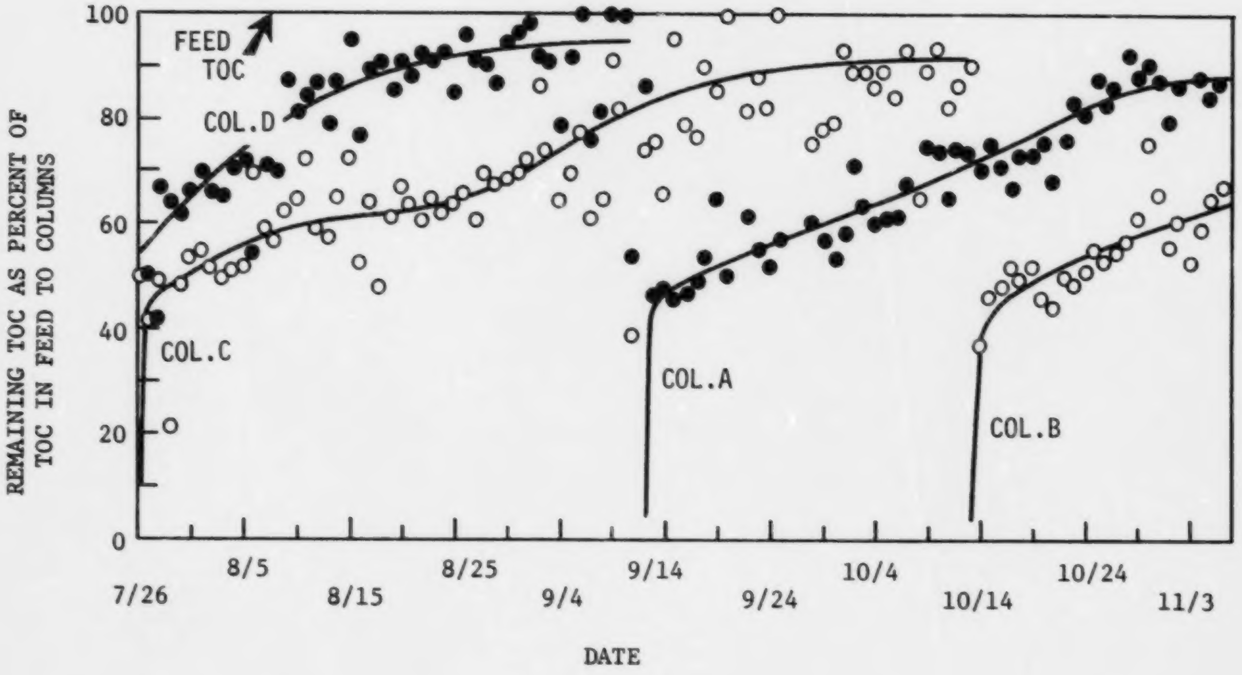


Figure 21. Remaining TOC in water from columns during lime-carbon sequence

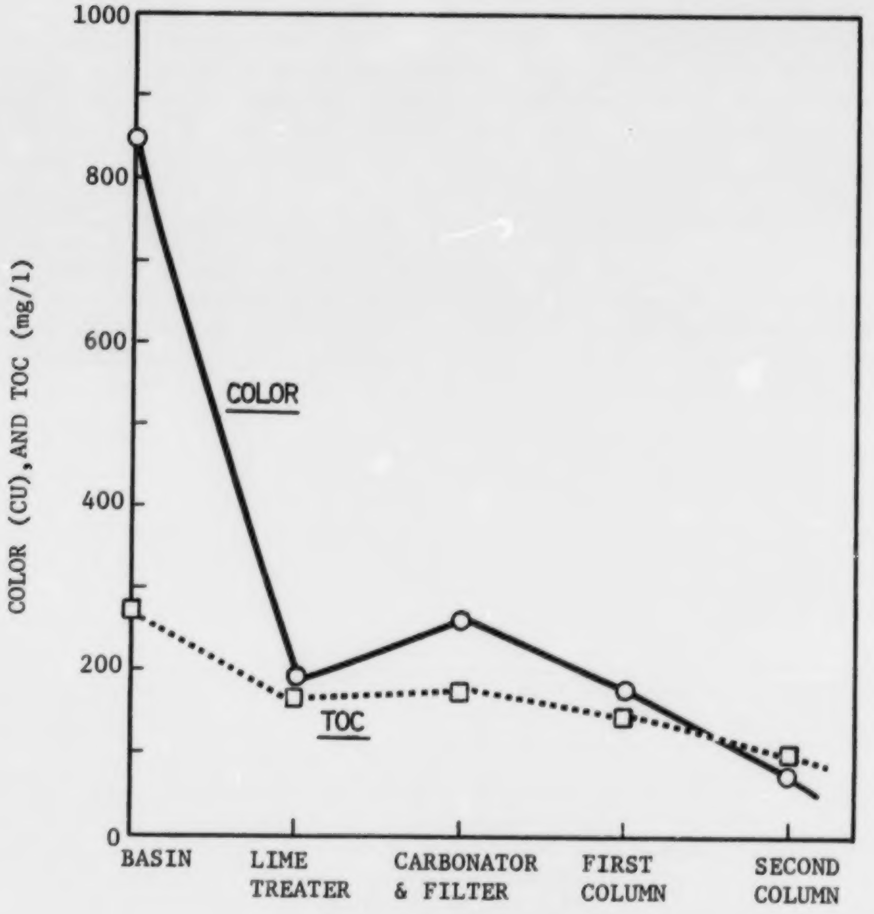


Figure 22. Color and TOC versus stage of lime-carbon treatment for medium calcium runs

RATES OF REMOVAL OF COLOR AND TOC

The average rates of removal of color and TOC are given in Table 30 for each column. The rates were almost doubled in going from the low-calcium runs to the medium-calcium runs. The rates for medium-calcium runs of 0.54 CU/g hr and 0.12 mg TOC/g hr were slightly greater than those of the high-calcium runs, but this increase was probably due to the higher feed concentrations during the medium-calcium runs.

At approximately equal concentrations, the rates of color removal in the lime-carbon column sequence were much greater than those of the bio-carbon and primary-carbon sequence, but the rates of TOC removal were much less than those for the bio-carbon and primary-carbon runs. However, in the comparison with TOC removal during bio-carbon, an adjustment of the reference concentration of TOC in the lime-carbon sequence by deducting the non-adsorbable organic solution (volatiles discussed later) results in more nearly equal TOC removal rates at equal adjusted concentrations.

The rates of removal of color and TOC were generally greater in the second column than in the first column even though the concentrations were much greater in the first column. It is possible that the carbon in the first column was subject to blinding by Ca-organics or residual high molecular weight color bodies, the latter also being suspected of that effect in the primary-carbon operations.

EFFECT OF OPERATING VARIABLES ON REMOVAL OF COLOR AND TOC

Effect of pH

The effect of pH at low and high levels of soluble calcium was investigated in a series of runs, each lasting several days. The purpose was to determine whether the beneficial effects of calcium on the lime-carbon sequence were enhanced or not by the high pH that was provided by lime treatment. It is generally recognized that the color intensity and the solubility of the color bodies of kraft mill effluents are increased by adjusting the pH from the normal level of 8-10 to a pH of 12. Therefore, one might expect that adsorption of color bodies by carbon at a high pH of 12 to 12.5 would be poorer than at a lower pH. Also, carbon adsorption of organics in general is generally thought to be better at lower pH levels.

These pilot plant tests showed that good carbon adsorption performance was obtained at pH 11.7, or greater, when the calcium content was greater than about 60 mg/1 and that adsorption remained good when the pH was reduced to 8-9 if the calcium content remained above about 60 mg/1. However, if the calcium content was reduced to the range of 7 to 23 mg/1 (the pH was 7-9), the carbon adsorption performance immediately became very poor.

A regression analysis of the data from 153 days of operation at a fairly wide range of conditions showed that color and TOC removals were influenced only slightly by changes in pH and that an increase of pH tended to increase the percentage removal of color and TOC.

It therefore is apparent that pH is not a major determining factor of adsorption performance. Particularly the high pH normally associated with the preferred minimum dissolved calcium level of 60 mg/l (as discussed earlier for the microlime treatment) is not detrimental to good performance of the carbon columns, as might have been expected. Rather, the higher pH tends to improve column performance. Hence, if it is desirable to reduce the pH of the water before reuse or discharge, the water should be carbonated after carbon adsorption, rather than before. To avoid precipitation of $CaCO_3$, such pH adjustment should be taken to pH 9 or lower.

Effect of Feed Concentrations

The concentrations of color and TOC, as well as soluble calcium, in the feed to the columns were major determinants of product color and TOC and of rates of removal. The influences of independent variables on the dependent variables were analyzed by means of plots of all conditions and results as functions of operating days.

Further insight on the effects of one parameter on another were obtained from a regression analysis which utilized a computer program. The independent variables included in the regression analysis were concentrations in the feed of Ca, total inorganic carbon (TIC), pH, FPCU, standard color, TOC, the cumulative hours of operation of the second column since it was recharged with fresh carbon, and the cumulative removals of color in each column. The dependent variables were color, FPCU, and TOC from the columns, rates of removal of color and TOC, turbidity of product water, percentage removals of color and TOC, and the ratio of FPCU/TOC.

This regression analysis indicated that the parameters affecting color and TOC of the product water in the order of their contribution were color, FPCU, TOC and Ca of the feed, and hours of operation of the second column. This analysis showed that pH and cumulative removals were also factors, but the contributions of these variables were already explained by the related variables of calcium concentration and hours of operation since a new column was added. This analysis indicated that the rates of removal were primarily functions of the concentrations in the feed, the hours of operation since a fresh column was added, and the related variable of cumulative removals by the columns. The percentage removals were primarily influenced by hours operated (and cumulative removals) and by the calcium content of the water. The TIC (carbonate) concentration had an almost negligible influence on column performance.

CUMULATIVE REMOVALS BY CARBON

As discussed in Section X, it was estimated during the primary-carbon sequence of operation that about 30% of the color and TOC removed by the carbon was in turn eliminated from the carbon columns by the combination of backwashing of the columns and bio-activity in the columns. These measurements were not repeated during the lime-carbon operation, but it is believed that a similar portion of the color and TOC was removed by non-adsorptive mechanisms during lime-carbon operation. Therefore, the term cumulative "removals" is used rather than "loadings" to indicate the degree of saturation of the carbon.

The cumulative removals of color and TOC for each column of carbon are shown as a function of operating time in Figures 23 and 24. The average cumulative removals of the columns when discharged were 660 CU/g and 175 mg TOC/g. The slopes of these curves are directly proportional to rates of removal. As pointed out previously, the rate of removal at any given cumulative removal is almost entirely dependent on the concentrations of color and TOC in the feed to that column. (Other factors affecting rates are fixed in this case, such as flow velocity, amount of carbon used, and temperature.) On several days the columns actually released more color and TOC than they adsorbed, as indicated by the downturn of the curves of cumulative removal in Figures 23 and 24. These releases of color and TOC were caused by upsets in the lime treatment, such as a failure of the lime feeder during the night.

It is normally expected that loadings on carbon columns will reach about 60% of equilibrium loadings established in batch isotherms. The average loading expected in the first column on the basis of isotherms with lime-treated water (see Section XIII) hence would have been 60% of 350 CU/g, or 210 CU/g, at the average concentration of about 220 CU in the first column in the pilot plant. However, at 500 to 900 CU/g (Figure 23) the cumulative removals of the carbon columns when discharged were 140 to 260% of the isotherm loadings of 350 CU/g, or 240 to 430% of the loading that would normally have been expected. This difference between isotherm loading and cumulative removal is evidently due to removals of color by non-adsorptive mechanisms, discussed above, and in more detail in Section X. The magnitude of the apparent non-adsorptive removals is much greater in the lime-carbon sequence than was observed in the normal operation of the primary-carbon sequence.

The average isotherm loading for TOC was 130 mg/l at the average pilot plant feed concentration of 170 mg/l, and this value was exceeded by two of the last three columns in the lime-carbon operation (see Figure 24).

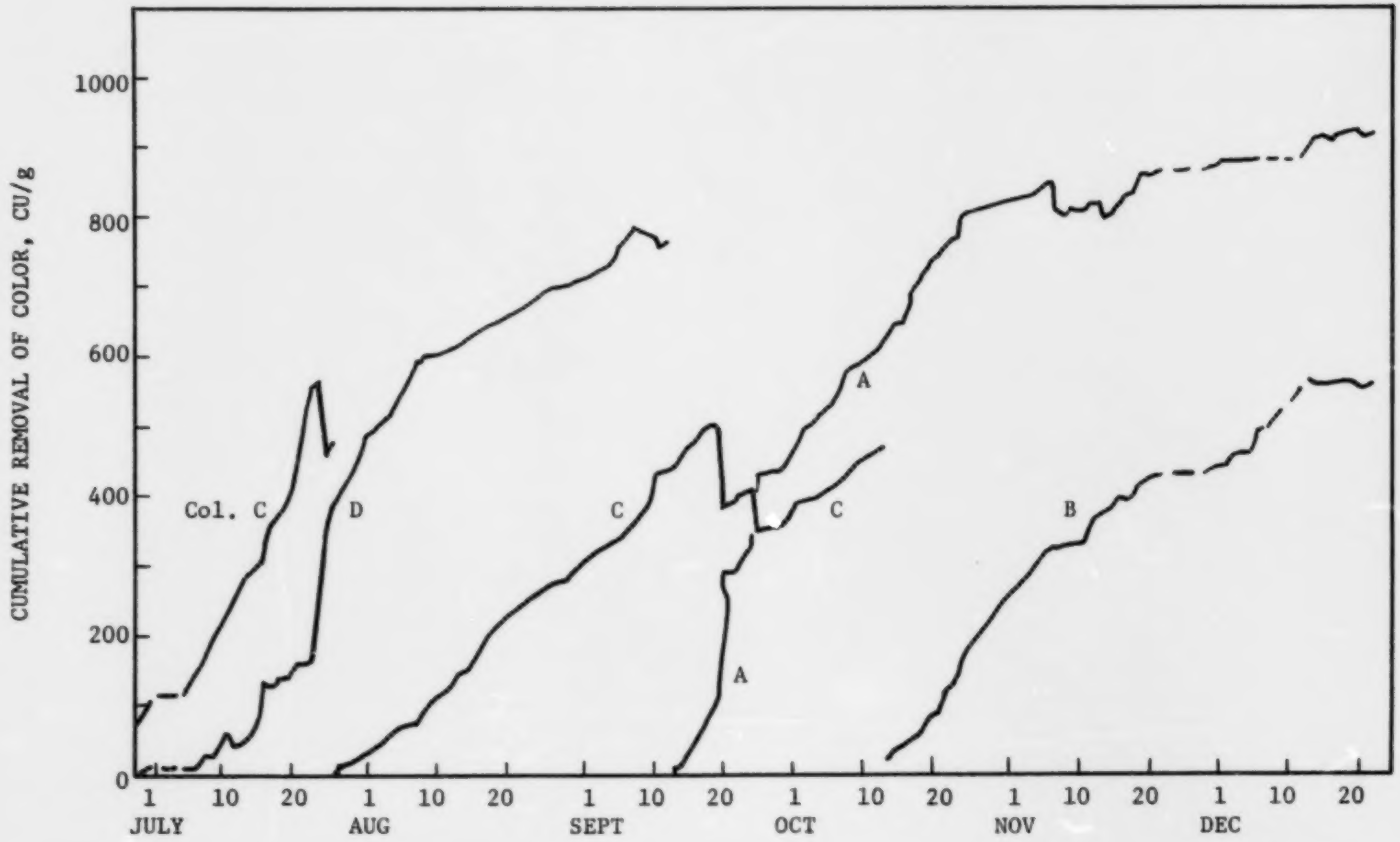


Figure 23. Cumulative removal of color versus time for lime-carbon operation

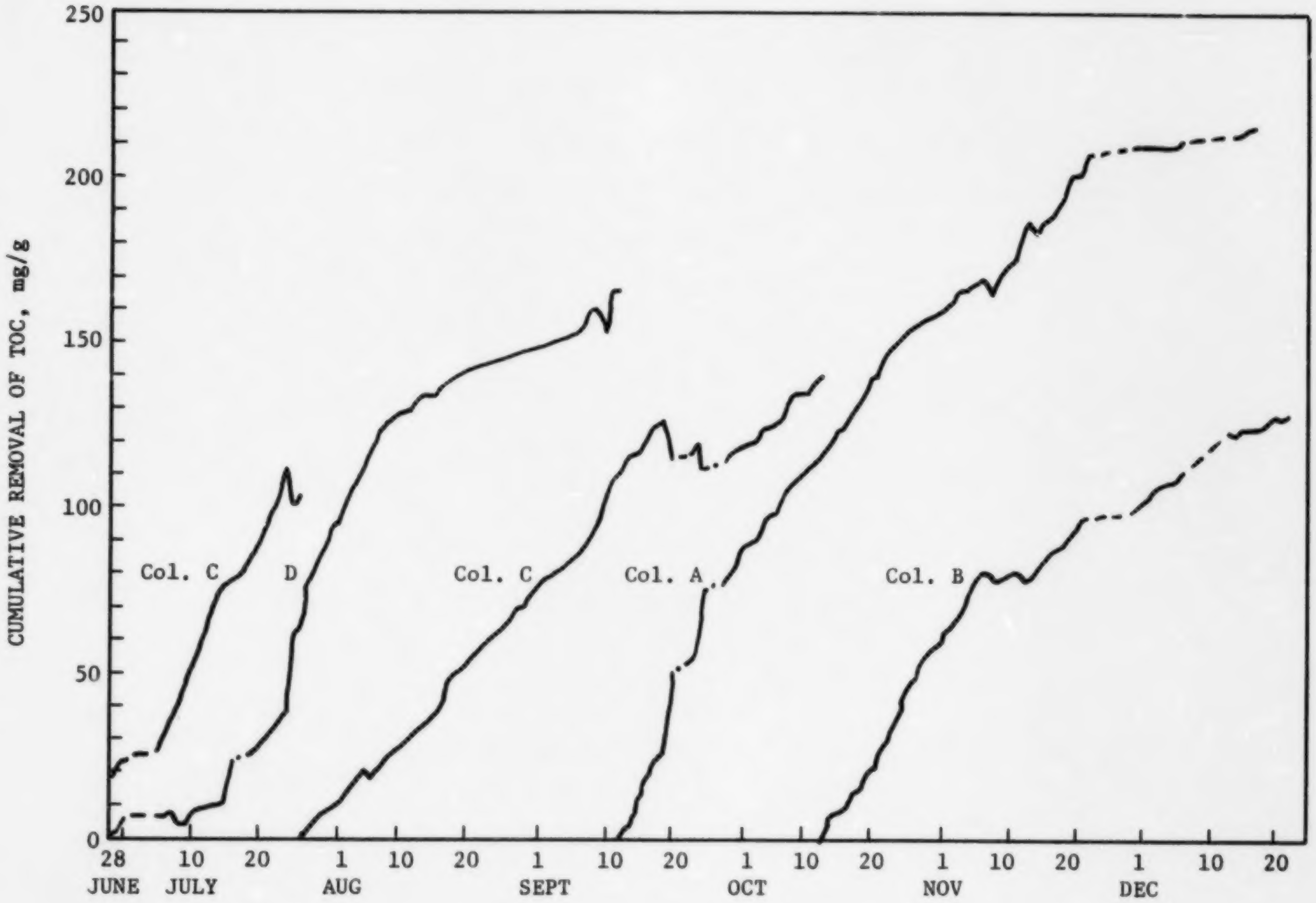


Figure 24. Cumulative removal of TOC versus time for lime-carbon operation

These cumulative removal curves show that the lead column when taken off-line was removing color and TOC at a fairly good rate. Therefore, the lead column could have been left on line for a longer period except that a fresh column was needed to maintain low values of color and TOC in the discharged water. In designing a commercial plant, the savings in regeneration costs by using more columns in series must be balanced against the greater fixed costs in providing the additional length of carbon bed.

REMOVAL OF LOW MOLECULAR WEIGHT COMPOUNDS

A large portion of the TOC remaining after carbon adsorption was made up of low molecular weight organic compounds, which are not readily adsorbed by activated carbon. The average concentrations of identifiable compounds during the lime-carbon operation are given in Table 31.

Table 31. ORGANIC COMPOUNDS IN LIME-CARBON OPERATIONS

	To carbon columns	From carbon columns
Methanol, mg/l	37	37
Ethanol, mg/l	trace	trace
Acetaldehyde, mg/l	19	18
Acetone, mg/l	10	14
Formic acid, mg/l	9	6
Acetic acid, mg/l	70	79
Total identified volatiles, mg/l	145	154
TOC of total identified volatiles, mg/l	60	65

Each value is an average from 8-12 analyses. The concentrations of some of these volatiles varied with time. For example, the acetaldehyde concentrations were 30-45 mg/l in August and September, 1972, were 0-11 in October and November, 1972 and 11-14 later in November, 1972. As discussed in Section VII on Clarification and Bio-oxidation, it is believed that much of the acetic acid was formed by anaerobic activity in the equalization basin. These volatiles apparently contributed about 65 mg/l of the 100 mg/l of TOC in the lime-carbon product water.

REMOVAL OF BOD AND TURBIDITY

As computed from the data in Table 29, the removals of BOD were generally low in the carbon columns, ranging from 13 to 40% of the BOD in the feed to the columns. The overall removals of BOD in the lime-carbon treatment ranged from 22 to 45% for the periods grouped by calcium levels. The low removals of BOD can be readily understood by the relatively high concentrations of hard-to-remove, low molecular weight compounds discussed above, which are all bio-degradable.

Turbidity was contributed mainly by insoluble calcium-organic compounds. As shown in Table 29, the turbidity of the water to the carbon columns was lower in the medium-calcium runs than in the high- and low-calcium runs. The columns removed 60% of the turbidity at the medium-calcium content and 86% of the turbidity at the high-calcium content. A regression analysis of the lime-carbon data showed that the turbidity of the carbon-treated water was directly related to hours of operation of the second column since it was added as a fresh column, indirectly related to calcium concentration (and the associated parameter of pH), and directly related to the filter paper color of the feed water.

REMOVAL OF METAL IONS

On the basis of 16 sets of samples, the average soluble calcium content of the water to the columns was reduced in passage through the columns by 3 mg/1 from 80 mg/1 to 77 mg/1. The amount of total calcium removed, including that in colloidal calcium-organic compounds or calcium carbonate, was probably greater, but it was not determined.

Other metal ions to and from the columns were determined by analysis of from one to six samples by atomic absorption after filtration of the sample through a 0.8 micron Millipore filter. The average results of these analyses are given in Table 32. Most metal ion concentrations were affected very little by carbon adsorption. Only manganese and potassium were removed to an appreciable extent.

Table 32. METAL ION CONCENTRATIONS IN LIME-CARBON SEQUENCE

Metal	No. values averaged	Concentration, mg/l to lime treater	to columns	from columns
Ca	16	13	80	77
Mg	6	1.6	0.3	0.36
Al	5	2.0	1.5	2.6
Fe	6	0.36	0.30	0.34
Mn	6	0.28	0.14	0.03
Zn	5	0.13	0.07	0.06
K	1	12	12	3.5
Na	1	309	327	-
Cu	4	0.03	0.04	0.03
Ni	4	0.5	0.6	0.6
Ti	1	0.5	0.4	-
Si	1	7.6	7.3	-

PRESSURE DROP AND BACKWASHING OF COLUMNS

The lime-treated water that was used in the carbon columns was filtered through the duomedia filter to remove as much of the suspended solids as possible. The turbidity of lime-treated water was reduced by the filter from about 60 to 45 JTU or by 15 JTU. The turbidity was further reduced by the columns to 12 JTU in the medium-calcium runs and to 7 JTU in the high calcium runs.

The columns were backwashed every two days throughout the lime-carbon operation. The pressure drop across the first column just prior to backwashing averaged 4 psi and across the second column averaged 2 psi. The average pressure drop across both columns (20 ft of carbon) during operation was about 2 psi. The pressure drop did not increase with the length of time a given column was in service. There was no evidence of calcium sludge deposits in the column after backwashing, as determined by inspection of the carbon when discharged from a spent column.

During the first several weeks of the lime-carbon sequence, the columns were backwashed with well water that had very little hardness, high bicarbonate content, and a pH of 4-5. When the first spent column was removed, we found that the lower two feet of the carbon was cemented together with deposits of calcium carbonate. Evidently the high carbonate content of the wash water formed the calcium carbonate from the calcium in the lime-treated water which was at a pH of about 12. Thereafter, product water was used for backwashing and no further trouble was experienced with carbonate deposits.

SECTION XII

OPERATING RESULTS:

LIME-FACET ADSORPTION

OBJECTIVES AND DESCRIPTION OF OPERATION

The FACET carbon adsorption system was under development in short-term runs in the pilot plant prior to May, 1972. Continuous operation of the unit was started on May 15, 1972, with a feed of lime-treated water. After two weeks of operation, the FACET unit was shut down for the next four months to give more attention to the lime-carbon column operation. The FACET unit was then operated seven days per week from September 28, 1972 to December 7, 1972, with lime-treated water at 10 gpm. During these periods of operation, techniques were perfected to give good control of slurry concentrations in the FACET tanks and to give uniform rates of transfer of carbon as a slurry of 10-15% solids from one tank to the next and of discharge of spent carbon. The carbon feeder gave reliable and consistent delivery of fresh carbon from the feeder storage hopper to the third FACET tank (third in the direction of water flow). A flow diagram for the FACET system is given in Figure 6.

RESULTS FROM FACET OPERATION WITH LIME-TREATED WATER

There were five operating periods of three to five days each in which the feed water to FACET remained fairly constant and which appeared to give results that are representative of the FACET operation. The conditions and results from these periods are summarized in Table 33. The five periods are designated as Runs A through E and are presented in chronological order. The average temperature of the water was 85°F.

The conditions of operation that have a major effect on removals of color and TOC include the concentration of color and TOC in the feed, concentration of soluble calcium in the feed, carbon slurry concentration, carbon feed (or dosage) rate, and turbidity and suspended solids of the feedwater. The concentration of suspended solids and color in the feedwater varied greatly as a result of unstable conditions in the lime treatment step. Quite often, a color increase in the water from lime treatment caused a much greater percentage increase in the color from the FACET treatment.

The carbon transfer rates given in Table 33 under "Feed" are the rates to the third tank, and the rates under the tank numbers are the rates of transfer from each tank. The rate of discharge of spent carbon from the system is that given as discharge from the No. 1 tank. All weights of carbon, including the feed, are on an oven-dried basis.

Table 33. RESULTS FROM FACET OPERATION WITH LIME-TREATED WATER AT 10 GPM

Run no.	A				B				C				D				E				Avg.C, D, E[b]			
Dates	5/15-5/18/72				5/23-5/27/72				9/28-9/30/72				10/3-10/6/72				10/26-11/6/72							
Length, days	3.3				5				3				4				12				19			
Tank no.[a]	Feed or Total	1	2	3	Feed or Total	1	2	3	Feed or Total	1	2	3	Feed or Total	1	2	3	Feed or Total	1	2	3	Feed or Total	1	2	3
Carbon rate lb/hr	16.3	23	16	14	9.2	8.6	8.1	8.3	2.1	3.6	3.2	2.4	1.8	2.5	2.0	1.4	2.7	1.7	1.8	2.4	2.42	2.17	2.06	2.19
Carbon in tank, g/100 ml	10.3	19	11	10	6.8	6.2	7.0	7.3	12.2	14.5	12.7	9.5	11.7	12.6	12.7	9.7	14.3	14.0	13.5	15.5	13.4	13.7	13.2	13.3
lb	543	258	150	135	274	84	173	98	517	204	179	134	493	178	179	137	605	197	190	218	567	194	186	188
Lime to lime treater mg CaO/l	600				610				490				470				670				600			
Soluble Ca to FACET, mg/l	101				140				77				136				153				137			
Color, FPCU	1090	807	691	746	885	783	846	617	1086	952	1317	993	581	1055	820	922	872	1022	1055	741	844	1018	1047	819
CU	250	88	63	48	266	163	111	55	264	196	126	58	160	152	95	74	157	166	100	73	174	167	103	71
Color removed, % of feed	81	65	10	6	79	39	19	21	78	26	26	26	54	5	36	13	53	-6	42	17	59	4	37	18
Color removal rate, CU/(g hr)	1.8	3.1	0.8	0.5	3.9	6.2	2.8	2.9	2.1	1.7	2.0	2.5	0.86	0.23	1.59	0.77	0.71	-0.23	1.74	0.62	0.96	0.17	1.75	0.95
TOC, mg/l	151	83	70	70	162	130	96	90	168	116	98	82	140	131	101	87	158	154	132	101	156	143	120	95
TOC removed, % of feed	54	45	9	0	45	20	21	4	51	30	11	10	38	6	22	10	36	2	14	20	39	8	15	16
TOC removal rate, mg/(g hr)	0.75	1.3	0.4	0	1.3	1.9	1.8	0.3	0.78	1.23	0.50	0.60	0.53	0.25	0.84	0.51	0.46	0.10	0.57	0.71	0.54	0.33	0.62	0.66
pH	11.8			11.7	12.1			12.0	12.0			12.1	12.3			11.9	12.1			12.0	12.0			12.0
Suspended solids, mg/l	370			411				162								250				416				280
Turbidity, JTU									25				25				40							
BOD, mg/l									242								266			146				
Ratio, FPCU/CU	4.4	9.2	11	15	3.3	4.8	7.6	11	4.1	4.9	10	17	3.6	6.8	8.6	12	5.6	6.2	11	10	4.9	6.1	10	12

[a] The results for tank 3 are for the water before it was filtered in the duomedia filter.
[b] The averages are weighted by the days of operation of each run.

REMOVALS OF COLOR AND TOC

Unusually low average values of color (48 and 55 CU) and TOC (70 and 90 mg/l) were obtained during Runs A and B. The good removals were probably mainly due to the high carbon feed rates of 9.2 and 16.3 lb/hr. At a much lower average carbon feed rate of 2.4 lb/hr (4.0 lb/1000 gal) during Runs C, D, and E (19 days), the color was reduced from 171 to 71 CU for a reduction of 59%, and the TOC was reduced from 156 to 95 mg/l, for a reduction of 39%.

Also included in Table 33 are filter-paper colors (FPCU) because this provides a measure of the amounts of colloidal color bodies resulting from the FACET treatment that are removed by the 0.8 micron filter used for standard color measurement. Most of the total (unfiltered) color of the FACET product water was removable by filtration through Whatman No. 2 paper or through the duomedia filter in the pilot plant. During Runs A and B, the FACET product water after the duomedia filter had filter-paper colors as low as 128 to 150 CU and standard colors in the range of 30 to 60 CU. During most of the remaining periods, the product water contained substantial amounts of colloidal color bodies that were not removed by the duomedia filter or by filter paper. It was noted that when the low filter-paper colors were obtained, the black color bodies normally in the water from the last FACET tank were sufficiently large that they would settle from the water when a sampe was left undisrupted in a beaker for about 20 minutes. We were unable to pinpoint the conditions of operation that would insure that the color bodies would always be of the size that would be removed by the duomedia filter. A high calcium content is believed to favor the growth or coagulation of the larger color bodies during FACET treatment. Even though the data of Table 33 do not show a very strong correlation between soluble calcium concentration and product water colors, other pilot plant data indicate that, in general, best removals of color were obtained with high concentrations of soluble calcium in the feedwater to FACET.

It was found that the ratio of filter-paper color (FPCU) to standard color (CU) is a useful indicator of the size distribution of the color bodies, and the average values of this ratio are given in Table 33. The values of FPCU/CU increased from about 2.0 in the feed to lime treatment to a range of 3.3-5.4 in the feedwater to FACET and to a maximum in the third tank in the range of 10-17. This increase indicates that most of the apparent color was in the range larger than the 0.8 micron size by the time the water was discharged from the third tank. An experimental program, discussed in Section XIII, indicates that some of the color bodies in the product water that were larger than 0.8 micron were peptized carbon, while some were coagulation products of color bodies originally in the water. The exact contribution of each was not determined.

The average TOC concentrations of the FACET product water during Runs A-E ranged from 70 to 101 mg/l, and the percent removals of TOC from the feedwater to FACET ranged from 36 to 53%. As would be expected, the best removals of TOC occurred in Runs A and B which had high carbon feed rates.

The values of TOC concentrations in the product water are believed to be much higher than they would have been if it had not been for the low molecular-weight compounds formed in the equalization basin by anaerobic activity, which was discussed in the section on the primary-carbon sequence (Section X).

The percentage removals of TOC and color by each stage varied widely from one run to another. During Runs A and B with a high feed rate of carbon, most of the color and TOC was removed in the first tank. These results at the high carbon feed rate indicate that the color and TOC remaining after the first stage was poorly adsorbed, even with relatively fresh carbon. At the lower carbon feed rates of 1.8 to 2.7 lb/hr during Runs C, D, and E, a large portion of the total reduction of color and TOC occurred in the second and third stages, which indicates that the carbon feed rate was about the lowest that could be used. At the average carbon feed rate of 2.2 lb/hr for these runs, the dosage was 4.0 lb/1000 gal or 480 mg/l.

During Run E, on the basis of three sets of samples, the BOD was reduced from 266 mg/l to 146 mg/l, for a reduction of 45%.

ADSORPTION PERFORMANCE BY LIME-FACET COMPARED TO THAT BY LIME-CARBON COLUMNS

The rates of adsorption per unit weight of carbon in the system for FACET operation during Runs C, D, and E, are compared in Table 34 to those from microlime-carbon column operation at medium calcium concentrations. The rate of removal of color in lime-FACET was 0.96 CU/(g hr) versus 0.59 CU/(g hr) for the lime-carbon column operation, or 1.6 times as great. The rate of removal for TOC was 0.54 mg/(g hr) versus 0.14 mg/(g hr) for lime-carbon columns, or 4 times as great.

The results from these two modes of operation are not strictly comparable. For instance, the soluble calcium content of the FACET feed was higher (137 versus 86 mg/l). The feed concentrations and the amounts of color and TOC removed for FACET were less. The cumulative removals on the spent carbon were less for the FACET operation, i.e., 213 versus 668 CU/g, and 126 versus 263 mg TOC/g. The carbon dosage rate was greater for FACET (4.0 versus 2.2 lb/1000 gal). The feed to the lime-carbon columns was filtered through the duomedia filter, whereas the feed to FACET was not, which put an additional load of suspended organics on the FACET system. If the conditions in the FACET operation had been the same as

Table 34. COMPARISON OF LIME-FACET AND LIME-CARBON COLUMN OPERATION AT A WATER FLOW RATE OF 10 GPM

	Lime-carbon	Lime-FACET
Period used	Med. calcium	Runs C,D,E
Reference table	28[a]	33
Days of operation	30	19
Avg. soluble Ca, mg/l	86	137
pH	11.4	12.0
Carbon dose rate lb DWB/1000 gal	2.2	4.0
Contact time of carbon, days	97	10
Contact time of water, hr	1.77	0.84
Carbon in system, lb	2880	567
Mean particle size, microns	670	345
Color, feed, CU	252	174
product, CU	76	71
removed, CU	176	103
% removed	70	59
cum. removed, CU/g	668	213
rate, CU/(g hr)	0.59	0.96
TOC, feed, mg/l	177	156
product, mg/l	100	95
removed, mg/l	77	61
% removed	44	39
cum. removed, mg/g	263	126
rate, mg/(g hr)	0.14	0.54

[a] Values involving weight of carbon have been adjusted to dry-carbon basis.

in the carbon-column runs, it is believed that the FACET rates would have been lower but still substantially greater than those of the carbon-column runs.

This comparison at equal water flow rates show that the rates of removal with FACET were much greater, that the size of the contacting zone was only 11% of that for the columns, and the inventory of carbon was only 18% of that for the columns. The advantages of FACET over column adsorption are that it permits changing of dose rate of carbon to meet changing feed concentrations, it has ability to handle a feed with a high concentration of filterable solids, it requires no backwashing, it will require smaller and lower-cost equipment, it requires a smaller inventory of carbon, and it provides a continuous flow of carbon to regeneration.

Potential disadvantages of FACET include: it might have a greater attrition loss of carbon, it requires coagulation or filtration of the product water, and it requires more automatic controls to regulate slurry concentrations. In a commercial unit, a greater number of stages would be used which would permit a closer approach to true counter-current contacting, high cumulative removals by the carbon, and lower dose rates.

ATTRITION OF CARBON IN FACET OPERATION

One of the major concerns in considering FACET as a viable commercial process for treatment of water is whether attrition of the carbon particles in stirred contactors would cause excessive loss of carbon as fines in the product water. Data obtained to date indicate that loss of carbon will constitute a minor operating cost.

Ten tests were made in the laboratory to determine attrition losses by stirring slurries of Darco XPT in effluent water and in deionized water for periods of 6 hr to 5 days. In most of the tests the carbon sample was wet-screened through a 200-mesh sieve before and after the test, and the loss in weight of +200 mesh particles was usually defined as the attrition loss. Since it was found that the Darco XPT carbon has a high water-soluble content of 1.2 to 3.5%, the carbon sample was first water extracted to remove solubles. The attrition loss in the above tests was generally less than 1% when the carbon was stirred 4-5 days and the results calculated on weight of water-washed oven-dry carbon.

We attempted to determine attrition losses by measuring total losses of carbon from the FACET system during the pilot plant runs by means of weight balances over periods of about a week, but it was found that it was very difficult to get a reliable weight balance on this system. To get reliable data, the weight of carbon in the system at the start and end of the test period was needed but could not be measured with sufficient precision.

Another inaccuracy in making a weight balance was in measuring the rate of removal of spent carbon with sufficient precision.

The amount of filterable solids in the product water could not be used as a measure of attrition losses because the value of filterable solids in the feed water (about 300 mg/l) was as great as that of the product water, and both were difficult to determine precisely.

Some carbon was lost to the product water during the pilot plant runs due to some of the feed carbon to the third tank not being completely wetted which caused some particles to float and to be carried out in the overflowing product water. The clarification zone of this tank was later modified to prevent carry-over of fresh carbon in the product water.

SECTION XIII

SUPPORTING LABORATORY STUDIES

A large amount of laboratory work was carried out during the construction and operation of the pilot plant to provide information and guidance on changes in the pilot plant and to provide answers to problems that arose. A problem requiring the major effort was that of color increase in the treated water during certain conditions of carbon adsorption. Other laboratory studies included providing carbon adsorption isotherms of various streams throughout the pilot plant operation, determining best conditions of operation for lime treatment and carbon adsorption, and special analyses. The findings from these studies are summarized below.

COLOR INCREASE IN PRESENCE OF ACTIVATED CARBON

Laboratory evaluations and pilot plant runs of the FACET stirred-carbon adsorption system showed that there was generally an increase of color of unfiltered product water even though the TOC of the water decreased. In most cases, this apparent color was removed by filtering the water through a No. 2 Whatman filter paper or a sand filter in the pilot plant and was greatly reduced by filtering the sample through the 0.8 micron filter used in determining standard color. Since the "color" produced during contact of the water with stirred carbon was removed by the 0.8 micron filter, it was not "true" color but colloidal color. This increase of apparent color was also noticed in preparing adsorption isotherms, especially at low dosages of carbon of 0.2 to 0.5 g/l. The color that was removed from the carbon columns in the pilot plant during backwashing had much the same physical and chemical properties as that produced in the FACET tanks.

This increase of color was studied extensively in the laboratory because the formation of the colloidal color bodies would be expected to coat the external surface of the carbon. This would greatly reduce the rate of diffusion to the carbon pores and thus the rate of adsorption of the smaller molecules on the inner surfaces of the carbon in both the FACET and fixed-bed adsorption processes. It was desirable to learn how to control the formation of the colloidal color in the FACET system so that the colloids could be easily removed from the product water by sand filters or by coagulation. It was also hoped that knowledge of the mechanism of formation and the properties of the colloidal color would suggest improved modes of operation of the fixed-bed and FACET carbon adsorption systems or might lead to novel less-costly processes for coagulation and removal of color from pulp mill effluents.

The increase of color occurred whenever powdered or granular carbon was stirred for 1-4 hours with pulp mill effluent or synthetic effluent (dilute black liquor) if the ratio of initial color to external surface area of the particles was in the range of about 5,000 to 30,000 CU per square meter. Results of a representative experiment are shown in Figure 25. The color increase also occurred, at a much lower rate, when no carbon was present and occurred in presence of non-carbon granular solids and powders such as alumina, silica, diatomaceous earth, and pumice. The increase of color occurred with each type of carbon tested: Darco S-51 powder, Darco XPT 40 x 140, Darco 20 x 40, and Westvaco WVL granular. Most other brands of carbon exhibited the color increase at low dosages in the standard isotherm tests.

Temperatures up to 90°C increased the rate of formation several fold over that at 25°C. The rate of color increase was accelerated by increasing the pH over the range of 8 to 12. Heavy metal ions (which are present in the ash of the activated carbon and in the mill effluent) did not seem to affect the rate of color increase. The rate of color production decreased with time of stirring but was still significant after 4-24 hours.

An increase of solid carbon concentration in the water during stirring over the range of 0.3 to 100 g/l generally increased the production of color, but the rate of increase per weight of solid was greatest at low concentrations of solids. If the ratio of initial color to surface areas of the solid was outside of the range of 5,000 to 30,000, there was little increase of color.

The test conditions for maximum increase of color of pulp mill effluent were: 5-10 g/l of Darco 40 x 140 at 50°C for 1-4 hours. These conditions gave increases of about 700 unfiltered CU/g of carbon and 100 paper filtered CU/g.

The mechanisms causing this observed color increase were not pinpointed. The results of the various studies indicate that, as might be expected, some of the color is produced by carbon particles from the activated carbon that were originally present as dust or that were removed by attrition or by peptization in the presence of mill effluent. The remaining increased color was evidently produced from substances in the effluent itself.

The chemical and physical properties of the colloidal color bodies were studied by filtering the samples through filters of 2-0.05 microns, TOC analysis, microscopic observations, electron micrographs, ultraviolet absorption, infrared absorption, elemental analyses, and action of solvents, bleaching agents, and caustic. These studies showed that the color increase was due primarily to formation of black color bodies larger than 1 micron. As time of stirring increased, the concentration of "true" color passing 0.05 and 0.8 micron filters decreased, therefore there was

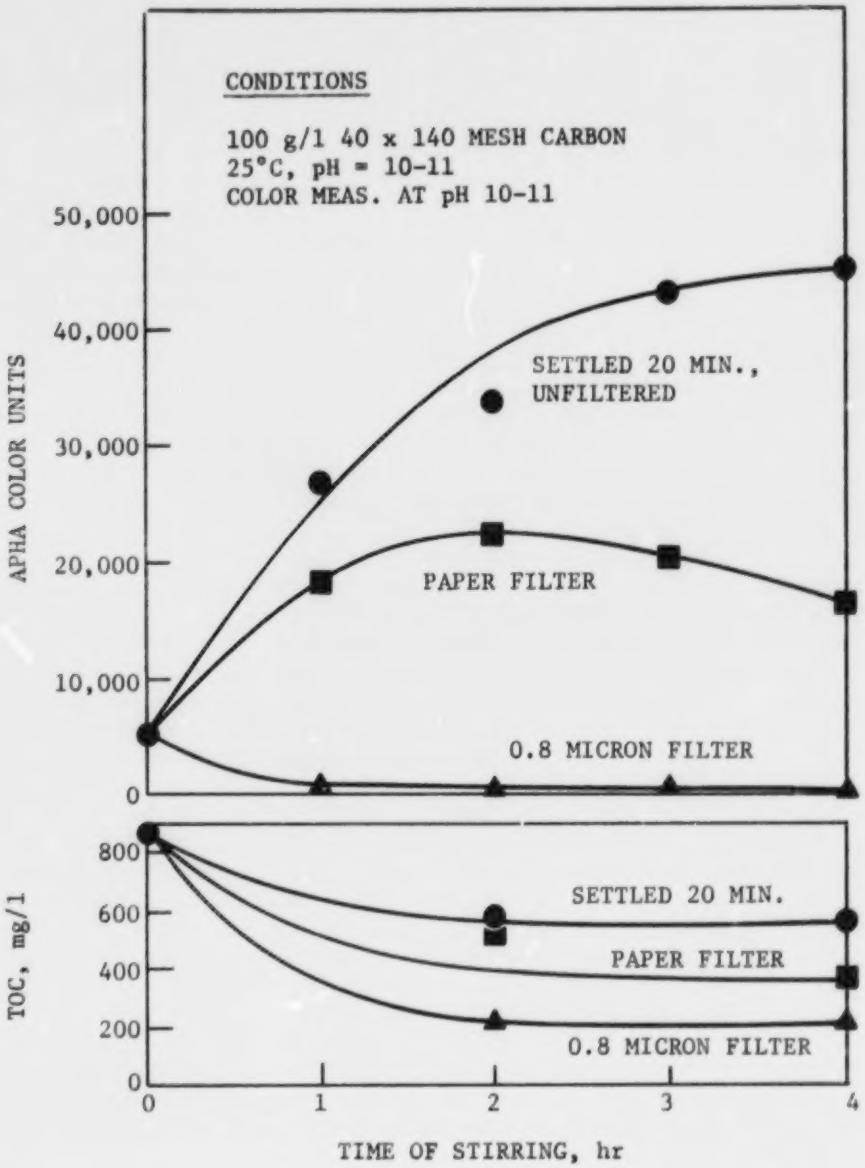


Figure 25. Changes in color of dilute black liquor with time of stirring with activated carbon

a shift from the small color bodies to the large colloidal bodies. The fraction of color removed by filter paper and 0.8 micron Millipore filters had very large concentrations of color per unit of TOC---- 25 to 50 times as great as that of mill effluent. The absence or presence of oxygen in a stirred test had no apparent influence on the degree of color increase. The color intensity of the color bodies from a color increase test was not reduced by treatment with hypochlorite or hot caustic, and the color was not extracted with methanol. Carbon stirred in water alone or with detergent present did not give appreciable color increases which indicated that attrition or peptization of the carbon were not major contributors to the color increase. However, digestion of carbon in dilute HCl at pH 2 caused significant color increase due to suspended black particles that were removable by an 0.8 micron filter and suggested that peptization of the carbon occurs under some conditions. Suspensions of activated carbon of up to about 2 micron size were found to give a 70% detection as TOC of the carbon actually present. Taken together with the observed high CU:TOC ratio, this point tends to suggest that the color increase was not from activated carbon particles.

A study of this problem by the Institute of Paper Chemistry (unpublished report) indicated that a portion of the color from the backwashing of carbon columns could be metal sulfides, that the color bodies after methanol extraction had "infrared spectra" (actually IR scatter, i.e., no distinguishing IR adsorption bands were seen in either sample) similar to those of activated carbon, and therefore the IPC concluded that colloidal carbon from the activated carbon was the primary source of the color of the backwash water.

Our studies have indicated that a substantial portion of the color increase is due to color bodies formed from the organic matter of the water in addition to that possibly contributed by the activated carbon. Possible mechanisms include (1) destabilization of organic colloids by contact with the carbon surfaces or after adsorption on the carbon (it appears reasonable to assume that at least a portion of the effluent color bodies is present in colloidal form, similar to lignin color in natural waters (1,2), particularly in view of the high molecular weight determined recently (43)), (2) formation of metal sulfides and metal-organic complexes at the surface of the carbon that become filterable colloids, (3) oxidative condensations to form insoluble compounds of lignin, as hypothesized by Ganczarczyk (39) in bio-oxidation of pulp mill effluents, (4) free-radical polymerization of lignin degradation products (42) and (5) other condensation products from hydrogen bonding and other types of chemical bonds.

This study of color increase of pulp mill effluents in contact with carbon under certain conditions has shown that the mechanisms causing it are very complex and that methods of controlling it for improving color removal by carbon are elusive. The study of this phenomenon is being continued by St. Regis Paper Company.

ADSORPTION ISOTHERMS

Equilibrium isotherms were prepared using Darco S-51, Darco 20 x 40, and Darco XPT 40 x 140 (all pulverized to less than 325 mesh) with samples of water from each step of treatment used in the pilot plant. Color and TOC isotherms were prepared using 43 samples of water. Average isotherms for each treatment step are given in Figure 26 for color and in Figure 27 for TOC. Average loadings from the isotherms for selected remaining concentrations of color and TOC are given in Table 35. The procedure used in making the isotherms is given in the Appendix B.

There was a considerable spread of loadings at a given color for a given stream, probably because of differences in the chemicals present from one sample to the next. The average loadings shown in Table 35 and Figure 26 indicate that with Darco carbon the greatest equilibrium loadings (at given concentrations) of color were obtained with water from lime treatment, lime-carbon, and bio-oxidation, but much lower color loadings were obtained with water that had passed through the retention basin and primary-carbon adsorption. The highest loadings of TOC at concentrations above 80 mg/l were with bio-oxidized water, retention basin water, and lime treated water.

Table 35. AVERAGE EQUILIBRIUM LOADINGS ON CARBON

FROM ISOTHERMS PREPARED DURING PILOT PLANT OPERATION[a]

Water Source	No. isotherms averaged	Loading on carbon, CU/g			TOC loading on carbon, mg/g		
		at 100 CU	500 CU	1000 CU	at 80mg/l	100mg/l	150mg/l
From mill ditch	7	186	345	857	29	41	61
From reten. basin	14	87	290	450	30	47	144
From P-C cols.[b]	4	87	207	-	21	33	70
From lime trt.	7	179	318[c]		27	63	116
From L-C cols.	5	260	-	-	16	29	60
From bio-oxid'n	2	120	480	2600	58	73	112
From B-C cols.	1	230	-	-	20	-	-

[a] Isotherms all with powdered Darco S-51, pulverized -325 mesh Darco 20 x 40, or pulverized Darco XPT 40 x 140.

[b] Abreviations: P-C = primary-carbon, L-C = lime carbon, B-C = bio-carbon.

[c] At 200 CU.

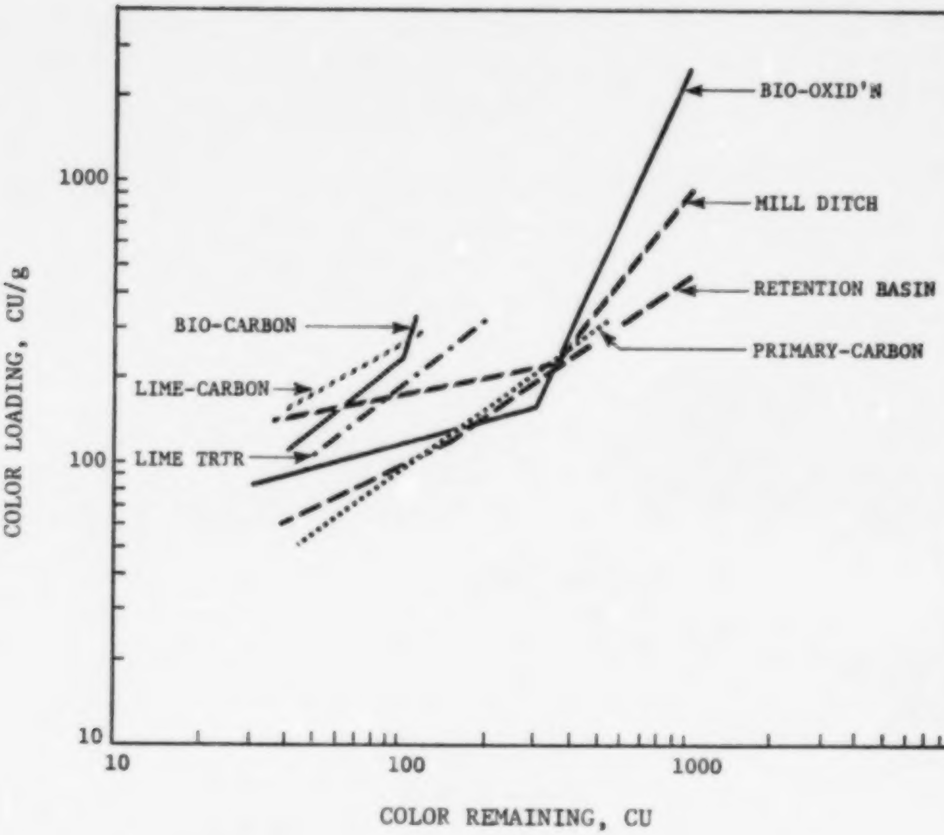


Figure 26. Average color isotherms after various treatments during pilot plant operations

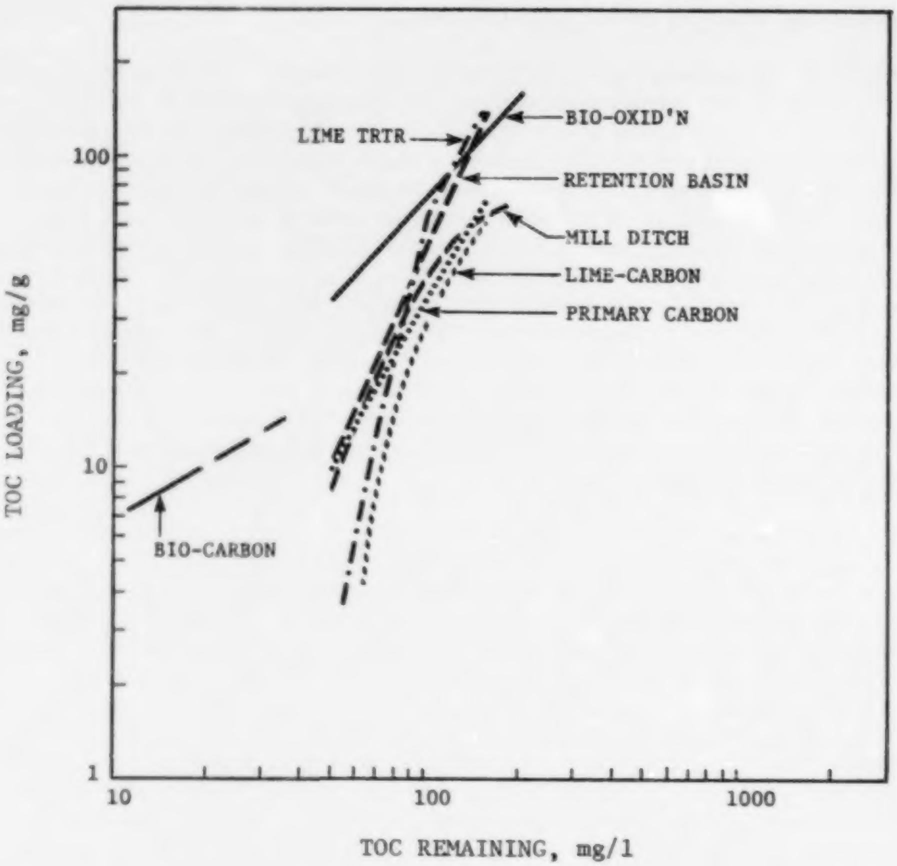


Figure 27. Average TOC isotherms after various treatments during pilot plant operations

The lowest TOC loadings were with lime-carbon and primary-carbon treated water. These average isotherms indicate that the color remaining after bio-carbon, lime-carbon, and lime treatments is more readily adsorbed than the TOC and could have been removed to a greater extent with greater retention time in the carbon columns.

The color isotherms generally have two slopes. At higher concentrations remaining after treatment the color loadings decrease rapidly with concentration, but at lower concentrations the loadings decrease less rapidly. In contrast, the TOC loadings are very sensitive to concentration remaining after treatment, with the bio-treated water being the least sensitive. The steep slopes of the TOC isotherms show that high loadings (above 30-80 mg/g) of TOC are achieved at concentrations greater than 100 mg/l but the loadings at less than 50 mg/l are very low, which indicates that it would be difficult to reduce TOC of mill effluents to concentrations of less than 50 mg/l, except after bio-oxidation. The steep slopes and the very low loadings of TOC obtainable at low residual TOC concentrations can be taken as an indication of the presence of very-hard-to-adsorb organic molecules. Actual chemical analyses presented in Sections X and XI show hard-to-adsorb, low molecular weight organics in the 40 to 80 mg/l of TOC range.

For all three treatment sequences, TOC isotherms obtained on effluent already treated with carbon show lower loadings (at given concentrations), particularly in the higher solution concentration range, than do isotherms of the corresponding sequences before carbon treatment. This observation is an indication that more readily adsorbed substances are adsorbed first, hence the solution remaining after carbon column adsorption are of a different qualitative composition, rather than being simply equally lower in concentration of each of the many compounds representing the measured quantities of TOC. This observation is of interest in conjunction with the discussions of rates of adsorption in Sections IX, X and XI. In the bio-carbon and primary-carbon sequences, adsorption rates decrease with decreasing concentration due to a reduction of driving force both from the reduction in concentration in solution and from the reduction in equilibrium loading at given concentration. On the other hand, in the lime-carbon sequence, rates in the second column, at lower effluent concentration, are actually higher than in the first column. This is contrary to expectations and is perhaps an indication of extensive blinding of the carbon surfaces in the first column from calcium-organic deposits.

The color adsorption isotherms before and after carbon column adsorption show an opposite relationship to that observed for TOC. A possible explanation for this phenomenon may be found in the known (43) wide distribution of molecular weight (up to 64,000 MW) of color bodies in kraft effluent before carbon treatment. Removal of color bodies in the high molecular weight ranges from the original effluent may be predominantly in the very large pores and on the external surface of the carbon, making the majority of the smaller pores inaccessible. Once the high molecular weight fraction is removed and fresh carbon is brought into contact with the solution, the lower molecular weight materials (perhaps in the 500 to 2,000 MW range) have ready access to the full range of carbon pore sizes and adsorptive area. This hypothesis is perhaps supported by the higher loadings obtained in lime treated water as compared to non-lime treated water. Lime treatment of unbleached kraft effluent has been found (43) to remove high molecular weight color bodies in preference to lower molecular weight color bodies.

Isotherms were used in checking the adsorption characteristics of several lots of Darco 20 x 40 and XPT 40 x 140 received for use in the pilot plant. Isotherms made with pulp mill effluent showed that the granular forms of Darco achieved slightly greater loadings of color and TOC at given concentrations than S-51 when all were pulverized to pass a 325 mesh sieve.

DYNAMIC VERSUS EQUILIBRIUM CONCENTRATIONS IN PILOT PLANT COLUMNS

Several tests were made in the pilot plant to determine how close the color and TOC concentrations in the carbon columns determined during normal operations (dynamic concentrations) approached the equilibrium concentrations for possible use in an evaluation of measured adsorption rates. These tests were made by shutting off the flow of water through the columns and then removing samples of water from the base of each column at intervals of time up to four days. After about 8 hours, the concentrations had almost reached equilibrium values. These tests indicated that the columns were operating at color concentrations 30 to 100% higher than the equilibrium values and at TOC concentrations 30 to 80% higher.

FOAMING TENDENCY OF TREATED EFFLUENT

The effect of the various steps of treatment on the foaming of the water by a standard foaming test was checked on 10 samples over a 6-month period. These tests indicated that the foaming of the mill effluent increased 50 to 100% during passage through the retention basin, without aeration. Lime treatment reduced the foaming of the feed water about 50%. Carbon adsorption by columns or FACET removed almost all of the foaming tendency.

EFFECT OF OPERATING CONDITIONS ON ADSORPTION OF COLOR AND TOC ON CARBON

Effect of pH

The effect of pH of the feed water on adsorption was investigated in several isotherm tests with mill effluent adjusted to pH values of 3 to 12. Within the range of 5-12, the results were inconclusive. Loadings varied as much as two-fold between different pH levels for specific samples, evaluated at a given color level. Results from test to test and color level to color level, however, were largely contradictory to each other. The limited amount of testing leaves the question of pH effect unresolved. At pH levels of less than 4, the lignin compounds become much less soluble and "loadings" (including precipitation) in the carbon increase sharply.

Effect of Temperature

A limited number of isotherms prepared at temperatures of 75° and 130°F with Darco S-51 and Westvaco AN and mill effluent indicated that the higher temperature gave about twice the equilibrium loadings of color at a color concentration of 300 CU and 1 to 2.6 times as much loading of TOC at a concentration of 100 mg/1. No comparative isotherms were obtained to observe a possible temperature effect on bio or lime treated mill effluent. In the pilot plant, the operating temperature range was very narrow (74-85°F). Hence, no temperature effect was observed. The temperature effect deserves further study, particularly in view of the fact that mill effluent can be available as high as 130-150°F, thus requiring no added cost for heating if the temperature effect is to be exploited in a large installation. The plant design and cost studies presented in Section XIV are based on the pilot plant results obtained at 74-85°F.

SECTION XIV

TREATMENT PLANT DESIGN STUDIES AND COST ESTIMATES

OVERALL DESIGN CRITERIA

Engineering design studies were made for full-scale plants for treating unbleached kraft mill effluents by the lime-carbon and bio-carbon sequences to provide water suitable for reuse in the mill. These studies were carried out to provide a basis for comparative cost estimates and to illustrate the methods of equipment design and operating procedures that appear best on the basis of our pilot plant studies and results from other effluent treatment studies.

The design and cost studies were based on the conditions given in Table 36 and water compositions given in Table 37. The treatment sequences discussed in this section and resultant water qualities are also presented in Figure 28. These conditions were chosen as typical of new and older unbleached kraft pulp and paper mills in the south. It was assumed that the effluents will be from mills that have catch basins for spills and sudden discharges of highly contaminated water. With such control, it was assumed that the variation was such that for 90% of the time the maximum color would be less than 1320 CU and that the minimum color would be greater than 680 CU. With this degree of variation, the TOC concentration would remain in the range of 175 to 325 mg/l 90% of the time. It was assumed that the effluents from the older and new mills would have the same concentrations of color, TOC, and BOD, but that the older mills would have a 50% greater volume of effluent per ton of pulp production.

The compositions of effluent after the various treatment steps and sequences in Table 37 are based on results achieved in the pilot plant, particularly in terms of microlime and carbon treatment, and on results in mill scale practice of bio-oxidation and minilime treatment. For the sequences involving activated carbon, the target of reusable water quality was defined as 100 CU and 100 mg/l TOC, although better results were achieved in the pilot plant. For the microlime-bio and minilime-bio sequences, the final color is based on that achieved after lime treatment, although in both commercial operations of minilime-bio the color increases to substantially higher levels in the bio-oxidation ponds, resulting in levels of 250 to 500 CU. Color increases were also seen in the laboratory as discussed in Section IV.

No cost estimate is included for the lime-FACET sequence because it was felt that the status of development achieved in the FACET system was not sufficient to warrant an estimate of comparable precision to those

Table 36. BASES USED FOR DESIGN AND COST STUDIES

Case no.	Age of mill	Mill pulp capacity, tons/day	Effluent volume, gal/ton	mgd	Treatment sequence[a]
1	new	800	12,000	9.6	microlime-carbon
2	new	1600	12,000	19.2	microlime-carbon
3	older	800	18,000	14.4	microlime-carbon
4	older	800	18,000	14.4	prim-bio-carbon
4a	older	800	18,000	14.4	prim-bio-carbon[b]
5	older	800	18,000	14.4	microlime-bio
5a	older	800	18,000	14.4	microlime-bio[b]
6	older	800	18,000	14.4	minilime-bio
6a	older	800	18,000	14.4	minilime-bio[b]
7	new	800	12,000	9.6	minilime-carbon
8	new	800	12,000	9.6	minilime only
9	older	800	18,000	14.4	minilime only
10	new	800	12,000	9.6	microlime only
11	older	800	18,000	14.4	microlime only

[a] Microlime and minilime treatments have no separate primary clarification.

[b] Estimate excludes capital cost of bio-oxidation facilities.

Table 37. AVERAGE COMPOSITION OF WATER TO AND FROM TREATMENT[a]

	Color, CU	TOC mg/l	BOD mg/l	pH
From mill to treatment	1000	250	250	10.5
From microlime	300	150	225	11.5
From minilime	150	135	187	8
From bio-oxidation	1000	175	25	8
From microlime-carbon	100	100	150	8
From minilime-carbon	100	100	117	8
From bio-carbon	100	100	20	8
From microlime-bio	300	70	20	8
From minilime-bio	150	50	20	8

[a] Other Properties:
Temperature: lime-carbon = 100°F., bio-carbon and bio-lime = 90°F.
Conductivity: minilime-carbon = 1200 micromhos, microlime-carbon = 3600 micromhos.

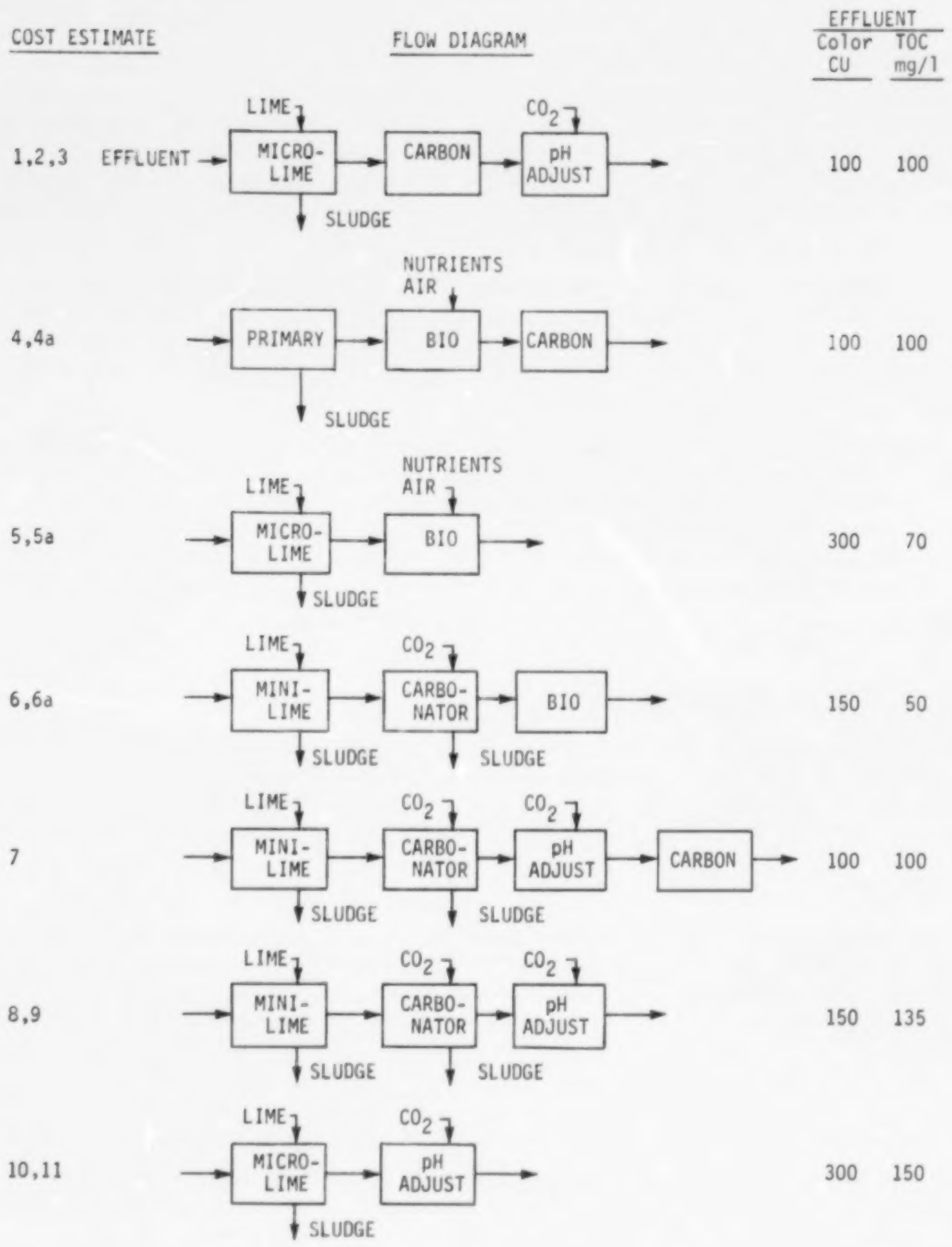

COST ESTIMATE
FLOW DIAGRAM
EFFLUENT
Color CU
TOC mg/l
1,2,3
EFFLUENT
LIME
MICRO-LIME
SLUDGE
CARBON
CO_2
pH ADJUST
100
100
4,4a
PRIMARY
SLUDGE
NUTRIENTS AIR
BIO
CARBON
100
100
5,5a
LIME
MICRO-LIME
SLUDGE
NUTRIENTS AIR
BIO
300
70
6,6a
LIME
MINI-LIME
SLUDGE
CO_2
CARBO-NATOR
SLUDGE
BIO
150
50
7
LIME
MINI-LIME
SLUDGE
CO_2
CARBO-NATOR
SLUDGE
CO_2
pH ADJUST
CARBON
100
100
8,9
LIME
MINI-LIME
SLUDGE
CO_2
CARBO-NATOR
SLUDGE
CO_2
pH ADJUST
150
135
10,11
LIME
MICRO-LIME
SLUDGE
CO_2
pH ADJUST
300
150

Figure 28. Flow diagrams and water quality for Cost Estimates 1-11

presented. Substantial savings are expected, as indicated in Section V, in equipment and carbon inventory cost, partially off-set (to a lesser degree than indicated in the preliminary estimates of Section V) by increased carbon dosages. The lime-FACET system operating costs, including fixed costs, are expected to be lower by 10-15% or several cents per 1000 gal.

No estimate is included for the primary-carbon system. Rough estimates made on the basis of pilot plant results indicated costs to be well out of line with the other potential systems, primarily because of the high capital cost requirement as a consequence of long contact time requirements.

The influence of excluding the capital cost of pre-existing bio-oxidation facilities was determined for each estimate that included bio-oxidation. The influence of price of activated carbon ($0.27 and 0.10 per pound) was determined for most estimates that used carbon adsorption. The comparative costs for microlime alone and minilime alone were determined as were the incremental costs of carbon treatment following lime treatment.

DESIGN METHODS AND ASSUMPTIONS

In this part of this section, the design methods and assumptions are discussed as they apply to each treatment step. Further information applying to design can be found in the appendix. Detailed design calculations for Estimate No. 1 are given in Appendix J.

Primary Clarification

The design for primary clarification includes a mechanical clarifier in which the rise rate is 700 gpd/ft^2, in which no coagulants are added, and which produces a clarified water containing 50 mg/l of suspended solids. Also included were water lift pumps, sludge pumps, a sludge settling tank, and sludge filters. The dewatered solids are hauled to landfill.

Bio-Oxidation

Bio-oxidation was assumed to be provided by aerated basins that are typical of those used by St. Regis and other southern kraft pulp mills. It was assumed that bio-oxidation removes 90% of the BOD, 30% of the TOC, and none of the color of the water. Nutrients are added in the ratio of 5 lb of N and 2.5 lb of P for each 100 lb of BOD loading. Aerators are used at a ratio of 32 pounds of BOD in the water to bio-oxidation per hp-day.

Microlime Treatment

The design for the microlime treatment facilities is based primarily on the results from the pilot plant operation but also on the results from the Interstate Paper (18) and Continental Can (14) lime treatment plants. The lime treatment system includes all auxiliary equipment: conveyors from the mill's lime storage, a lime slaker, and a lime slurry feeding system that is controlled by instrumentation to provide 60-90 mg/l of soluble calcium in the lime-treated water when adding about 520 mg/l of CaO. Sensors are used in the lime-water mixing zone of the reactor-clarifier to measure the soluble calcium content and to provide a control signal to the lime-slurry feeder. Lime slurry at 10% solids is introduced into the mill effluent just ahead of the lift pump to the lime treater.

The lime treater is a standard reactor-clarifier with a central agitated mixing zone to provide a long retention time of 30 minutes. A solids concentration of 0.5 to 1.0% solids is maintained in the mixing zone. A reaction time of 10 minutes is adequate, but the 30-minute retention time and high solids concentration are used to dampen short-term (less than 2 hr) fluctuations of color load. Longer-term variations in concentration and flow rate are handled by varying the lime dosage rate to maintain the desired concentration of soluble calcium.

The lime treater has heavy-duty sludge rakes to handle the dense sludge. The sludge is pumped at about 15% solids to a 12,000 gal sludge settling and surge tank in which the sludge is concentrated to about 30%. The sludge is dewatered with a wire filter at a rate of 100 lb/hr dry solids per sq ft of filter area to provide a cake of about 70% solids which is conveyed to the mill's lime kiln feeder. The sludge was estimated to contain, on dry basis, about equal amounts of $CaCO_3$ and calcium-organics and a total of 43% calcium determined as CaO.

The loss of lime as soluble calcium in the treated water was estimated to be 21% of the lime added to the water in microlime treatment but only 2% in minilime treatment. An additional loss of 5% of the lime added was assumed in the handling of lime sludge and filtration. This total loss of lime was assumed to be made up by purchased lime; all other lime used was assumed to be recalcined lime from the lime kiln. It was assumed that the lime cake from effluent treatment is recalcined in an existing lime kiln. The percentage of added load to the kiln from microlime treatment was 8% and from minilime treatment was 21% in the case of new mills having 12,000 gal effluent per ton of pulp. As discussed below, the capital costs for lime treatment include a proportionate share of the lime kiln cost.

Minilime Treatment

The design for minilime treatment is based primarily on the results reported by Spruill (14) for the Continental Can Company's minilime treatment of 9 mgd of unbleached kraft total mill effluent. Also used in the design calculation were results from the St. Regis - EPA pilot plant program, from the Interstate Paper Company minilime treatment plant at Riceboro, Georgia (18) and from the Georgia Pacific Corporation plant for lime treatment of bleach plant effluent at Woodland, Maine (7,8).

The minilime treatment plant includes a lime feeder, lift pumps, sludge pumps, lime treater-clarifier, carbonator (with kiln gas), carbonator-clarifier, sludge dewatering, and conveyor to return lime sludge cake to the lime kiln. The lime treater and carbonator clarifier use a rise rate of 700 gpd/ft^2.

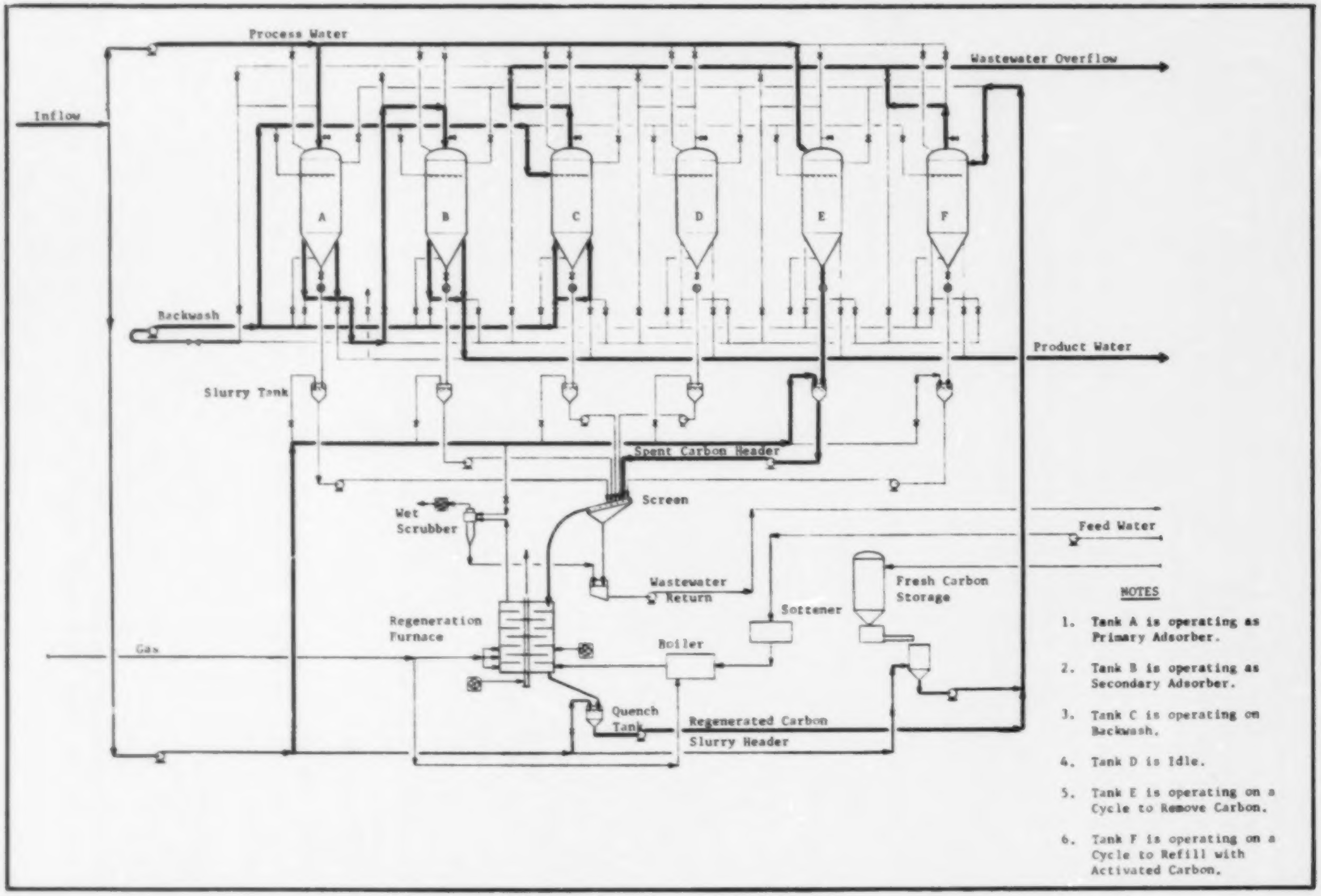
Additional information is given under microlime treatment (last paragraph).

Carbon Adsorption

The design for the carbon adsorption plants was based primarily on the results from the several modes of operation in the pilot plant. The arrangement of adsorption contactors or columns, the transfer of carbon as a water slurry, and the carbon regeneration unit were chosen to be similar to those used in the EPA report prepared by M. W. Kellogg Co. (17). In that report detailed designs and cost estimates were presented for treating by carbon adsorption 1, 10 and 100 mgd of municipal wastewater from biological treatment. These cost data are apparently the most reliable of the available costs on carbon adsorption and were chosen as the basis of the costs used in this report for carbon adsorption. A process flow diagram for that plant is given in Figure 29.

The design procedure is discussed below. Further information for the desgin of carbon adsorption plants is given in Appendix H, relationships useful in the designs of downflow carbon columns are given in Appendix I, while a detailed example is provided in Appendix J as part of Estimate No. 1, microlime-carbon treatment.

The total volume of carbon for a system was found by dividing the volumetric flow rate (volume of water per volume of carbon per hour) by the volume of water to be treated per hour. The volumetric flow


Process Water
Wastewater Overflow
Inflow
A
B
C
D
E
F
Backwash
Product Water
Slurry Tank
Spent Carbon Header
Screen
Wet Scrubber
Feed Water
Wastewater Return
Fresh Carbon Storage
Softener
Regeneration Furnace
Boiler
Gas
Quench Tank
Regenerated Carbon Slurry Header

NOTES

1. Tank A is operating as Primary Adsorber.
2. Tank B is operating as Secondary Adsorber.
3. Tank C is operating on Backwash.
4. Tank D is Idle.
5. Tank E is operating on a Cycle to Remove Carbon.
6. Tank F is operating on a Cycle to Refill with Activated Carbon.

Figure 29. Process flow diagram for FWPCA-Kellogg study (17)

rate is the inverse of contact time in hours. The contact time and volumetric flow rates were determined from pilot plant results for the feed and product concentration of each estimate. The superficial velocity and the cross-sectional areas of the columns were selected from pressure-drop considerations. The combined height of columns in series stems directly from the contact time required. It was assumed that the rate of adsorption would be the same as that in the pilot plant even though the rate is expected to be greater in the plant because of the greater flow velocity selected for the full-scale plant. The number of columns in series was selected to be at least three (to provide adequate counter-current contacting) and to maintain a reasonable height/diameter ratio and to keep the height at less than about 60 ft. The number of parallel trains was determined by the need to keep the height/diameter ratio between 1 and 2. Therefore, the diameter of the columns was fixed by the number of parallel trains used. In general, one additional column was provided for about every other train to handle excessive flows and concentrations of the feed. Two additional columns were provided, one being emptied of spent carbon and the other being refilled with regenerated carbon.

In operation, the lead (more nearly spent) column is removed from a train of columns when the quality of the water from the last column exceeds a tolerable level. A column of regenerated carbon is then added as the last column, and the carbon from the removed spent column is transferred as a slurry to the regeneration furnace. The regenerated carbon from the furnace is quenched in water and transferred to an empty column. When filled, this column is held in reserve to be used behind the last column temporarily whenever an overload to the system causes the product water to rise above a set tolerable level. This reserve column is put into regular service when the color or TOC concentration in the product water increases above the selected value and the first column of that train is removed from service for regeneration of the carbon.

Since the function of each column progresses through the series of columns, adequate piping and valving is provided to give the required flexibility.

The total inventory of carbon was determined from the number and dimensions of columns. The total inventory also included a 30-day supply of make-up carbon.

Backwashing of the columns requires a large flow of product water (5300 gpm in Estimate No. 1) for 15 minutes every day for the lead columns and every other day for the other columns. To minimize the loss of production due to this flow, the same water is used repeatedly for backwashing columns. In the lime-carbon sequences, the water is recycled to lime treatment after use for backwashing six columns.

Two clarifiers are provided to remove the suspended solids from the backwash water before each reuse. With this arrangement the loss of product water was only 0.8%. The off-time for backwashing reduced production by 3%, making the total loss of production 3.8%. An equivalent procedure limits the lost production due to backwashing in the bio-carbon treatment sequence.

The carbon regeneration unit must provide regenerated carbon at the dosage rate, which was 1000 lb/hr in Estimate No. 1. With an expected loss of 5% per regeneration cycle, the make-up rate with fresh carbon was 1200 lb/day. At the average regeneration rate in Estimate No. 1, one column is regenerated each 10.6 days.

The major design assumptions used in the cost studies for carbon adsorption are given below:

Carbon Columns - down-flow, fixed bed, 50% free-board (referred to carbon bed height).
Carbon Type - 20 x 40 mesh, equivalent to Granular Darco with bulk density of 25 lb/ft^3.
Flow Velocity - with lime-treated feed water = 4.2 gpm/ft^2, contact time = 1.8 hr, volumetric flow = 0.56 v/(v hr)
with bio-treated feed water = 4.0 gpm/ft^2, contact time = 4.4 hr, volumetric rate = 0.23 v/(v hr)
Excess Capacity- based on average feed rates after allowance for off-time for backwashing = 20 to 30% of normal flow rate or normal contaminant loadings in the feed water.
Backwashing - with air for 1 min and with water for 20 min at 10 gpm/ft^2. Lead columns are backwashed each day, others every other day. Backwash water is collected, clarified, and reused in backwashing more-contaminated columns, and then returned to lime treater. Water used is 1% of feed and off-time is 3% for a total loss of production of 4% for backwashing.
Filtration - no filtration is required for feed to columns.
Carbon Make-up - total loss from handling and regeneration of carbon is assumed to be 5% per regeneration. This rate of make-up was achieved in large-scale treatment of municipal effluent. In treatment of pulping effluents, it is reasonable to expect that some of the adsorbed organics will form activated carbon, which might cause a lower loss rate when regenerated.
Regeneration - spent carbon is transferred as a slurry, dewatered, and fed to a multiple-hearth furnace. A regeneration furnace capacity of 100 lb of carbon per day per square foot of hearth area is assumed and 25% excess capacity is provided.

COST ESTIMATES

Cost estimates were prepared for plants treating the effluent from unbleached kraft pulp and paper mills to show which items of capital cost and operating cost are the most critical or contribute the greatest amount to the overall operating costs, to show the effect of price of carbon on the costs, to show the effect of including in the capital cost of bio-carbon systems the cost of a new bio-oxidation unit or omitting this cost (for mills that have already amortized the unit), to compare the costs of microlime and minilime treatments, and to compare the costs of treating effluent from new mills and older mills (larger water usage per ton of pulp production).

Precision of Estimates

These estimates are believed to be within 20 to 30% of the actual costs. The costs of one estimate relative to another for the assumed conditions are expected to be much closer - probably within ± 10%. Since any particular mill will have a different set of conditions, the cost estimates would have to be revised to suit those conditions before a reliable cost for that mill can be obtained.

Bases of Estimates

The bases used in the design of the plants were discussed earlier in this section and are presented, in part, in Tables 36 and 37. Details of the assumptions used, the design procedures used, and method of estimating plant capital and operating costs are given in Appendix J for Estimate No. 1.

Capital Costs -

Capital costs are based on total plant costs for existing plants or on published costs from detailed cost studies. All costs were adjusted to January 1973 by use of the Engineering News Record Construction Cost Index.

The capital costs and some of the operating costs for minilime treatment are based on those of the 9 mgd lime treatment plant installed by Continental Can Co. in 1972 at Hodge, La., which was supported by an EPA grant (35). The costs are the actual costs for the complete installation including engineering and contractor's overhead and profit. Their costs were adjusted for a lower clarifier rise rate used in our estimates and for larger flow rates by use of 0.7 as the exponent of the ratio of flows.

The capital cost for microlime treatment was derived from the Continental Can cost data with adjustments made for eliminating the carbonation and final clarification step, for lower lime dosage, and for adding a final pH adjustment step. No pH adjustment step was added for the microlime-bio sequence.

The capital costs for carbon adsorption were derived from those prepared by M. W. Kellogg for EPA in 1969 (17) for 1, 10 and 100 mgd carbon adsorption plants for treating municipal effluent. Costs of each category of equipment of the Kellogg estimate were adjusted for the increased volumes of carbon needed and for other differences in our estimates, as illustrated in Appendix J.

The costs for primary clarification (for those estimates using biooxidation) were based on the costs for complete units for St. Regis mills.

The capital costs for aeration basins were based on the average costs for three installations; two St. Regis mills and a Crown-Zellerbach mill (36). These costs were adjusted for differences in flow rate by use of an exponent of 0.7.

Operating Costs -

The bases for operating costs are as follows:

Amortization - 6.25% of total cost of investment (TCI) per year.
Repair and Maintenance - 3% TCI/yr.
Taxes and Insurance - 2% TCI/yr.
Labor - On expected manpower requirements at $5.85/hr.
Plant Overhead - 75% of labor costs.
Steam - $0.80/1000 lb.
Fuel - $0.60/mil. Btu.
Electricity - $0.01/kWh.
Lime - Reburned - $12.40/ton CaO
Make-up - $24.23/ton CaO
Carbon make-up - $0.27/lb and $0.10/lb
Credit for treated water to replace mill make-up water = $0.06/kgal

RESULTS OF COST ESTIMATES

The capital and operating costs for new and older mills and for various treatment sequences are given in Table 38. The new mill was assumed to produce 12,000 gal of effluent per ton of pulp production and the older mill was assumed to produce 18,000 gal/ton. The quality of the water from both mills to the effluent treatment plant was assumed to be the same. The credit for treated water is based on typical mill water cost of $0.10/kgal less $0.04/kgal for pumping the treated water to the mill supply tank.

Table 38. COMPARISON OF COSTS FOR TREATING UNBLEACHED KRAFT MILL EFFLUENT

IN NEW AND OLDER MILLS BY VARIOUS TREATMENT SEQUENCES WITH CARBON AT $0.27/lb

Estimate No.	1	2	3	4	4a[a]	5	5a	6	6a
Pulp tons per day	800	1,600	800	800		800		800	
Effluent, gal/ton[b]	12,000	12,000	18,000	18,000		18,000		18,000	
Effluent, mil. gal/day	9.6	19.2	14.4	14.4		14.4		14.4	
Treatment	microlime -carbon	microlime -carbon	microlime -carbon	primary-bio-carbon		microlime -bio		minilime -bio	
Product water quality									
Color, CU	100	100	100	100		300		150	
TOC, mg/l	100	100	100	100		70		50	
BOD, mg/l	150	150	150	20		20		20	
Capital cost, $ million									
Lime trt. & pH adjustment	1.85	2.90	2.36			2.14	2.14	3.68	3.68
Carbon adsorption	4.90	9.00	6.98	11.92	11.92				
Clarifier & bio-oxid'n				5.09	2.39[a]	2.43	0.0[a]	1.82	0.0[a]
Total	6.75	11.90	9.34	17.01	14.31	4.57	2.14	5.50	3.68
Operating cost, $/kgal									
Fixed	0.217	0.191	0.200	0.364	0.306	0.098	0.046	0.118	0.079
Labor, o.h.,util.	0.075	0.064	0.069	0.127	0.127	0.032	0.032	0.049	0.049
Lime and chemicals	0.033	0.033	0.033	0.003	0.003	0.036	0.036	0.059	0.059
Carbon, at $0.27/lb	0.034	0.034	0.034	0.146	0.146				
Total op. cost	0.359	0.322	0.336	0.640	0.582	0.166	0.114	0.226	0.187
Operating cost, $/ton pulp	4.30	3.85	6.04	11.52	10.48	2.98	2.04	4.07	3.37
Operating cost with credit of $0.06/kgal for mill make-up water									
Net, $/kgal	0.299	0.262	0.276	0.580	0.522	0.106	0.054	0.166	0.127
Net, $/ton pulp	3.58	3.13	4.96	10.44	9.40	1.90	0.96	2.99	2.29

[a] Capital cost of bio-oxidation not included (for mills with existing bio-oxidation facilities)

[b] 12,000 gal/ton is for new mill, 18,000 gal/ton is for older mill

Microlime-Carbon, Large versus Smaller New Mills

Microlime-carbon treatment of effluent from a new 800-ton mill (Estimate No. 1) was estimated to require a capital investment of $6.75 million, of which $1.85 million is for lime treatment and pH adjustment and $4.9 million is for carbon adsorption. The operating costs were $0.36/kgal, or $4.30/pulp-ton, or $0.30/kgal and $3.58/pulp-ton including credit for water. The fixed costs for amortization, taxes, insurance, and maintenance amount to $0.22/kgal, or 60% of the total operating costs. When the mill capacity and effluent volume is doubled (Estimate No. 2), the capital cost is increased by 67% to $11.90 million and the operating cost is reduced to $0.32/kgal and $3.85/pulp-ton, or $0.26/kgal and $3.13/pulp-ton with credit for the water.

Microlime-Carbon, New versus Older Mill

The capital cost for an older mill (18,000 gal of effluent per pulp-ton) is $9.35 million (Estimate No. 3), or 38% greater than for a new mill (Estimate No. 1) having 12,000 gal/pulp-ton. The operating costs (before water credit) per 1000 gal for the older mill are slightly lower than for the new mill but are 40% greater per pulp-ton.

Primary-Bio-Carbon Sequence

The primary-bio-carbon treatment plant costs considerably more than the plant using microlime-carbon ($17.01 million for Estimate No. 4 versus $9.35 million for Estimate No. 3). The major share of this cost differencial is caused by the substantially higher cost of the carbon adsorption system ($11.92 million versus $6.98 million), the remainder of the differential is accounted for by the bio-oxidation system.

Estimate No. 4a is the same as Estimate No. 4 except that the capital cost of the bio-oxidation unit is not included in Estimate No. 4a. Even with no capital costs for bio-oxidation, the primary-bio-carbon sequence is 53% greater in capital cost and 74% greater in operating cost than the microlime-carbon sequence (Estimate No. 3). One advantage of sequences using bio-oxidation is that the BOD content of the product water is only about 20 mg/l as compared to about 150 mg/l for water from microlime treatment. It appears then for treating mill effluent for reuse that the bio-carbon sequences will be considerably greater in capital and operating costs than the lime-carbon sequence.

The cost of the primary clarifier is included in both Estimates Nos. 4 and 4a. To exclude the effect of an existing clarifier, the clarifier capital cost and its share of the fixed cost must be deducted from

Estimate No. 4a. It can also be seen that the capital cost for the primary clarifier in Estimate No. 4a is the same as that for the microlime treatment in Estimate No. 3. An existing clarifier may be used as part of a microlime treatment system and the costs adjusted accordingly.

Primary-Carbon Sequence

The pilot plant results indicated that the direct use of carbon adsorption after primary clarification would require a very long contact time (about 5 hr) in the carbon adsorbers to reduce the color from 1000 to 100 CU. Because of the indicated high cost of a plant using this sequence, an estimate for it was not included in these studies. However, rough approximations indicated that the capital cost for a 9.6 mgd plant would be about $15 to $20 million and that the operating costs would be about $0.70 per 1000 gal and $13 per pulp-ton. These costs indicate that other sequences involving carbon adsorption would be more economical.

Lime-Bio versus Lime-Carbon Sequence

Estimates Nos. 5 and 6 were prepared to determine whether effluent could be treated at lower cost by microlime or minilime followed by bio-oxidation, than by microlime- or minilime-carbon treatment. Microlime-bio would produce water having a color of 300 CU (or perhaps greater if there is an increase of color during bio-oxidation) which might make it unsuited for reuse. However, the capital cost (including bio-oxidation capital cost) is only $4.57 million, or 49% of that for microlime-carbon (Estimate No. 3) and the operating cost is $0.17/kgal, or also 49% of that for microlime-carbon. If a mill were to add microlime treatment ahead of an existing bio-oxidation unit at no capital charge for bio-oxidation (Estimate No. 5a), the capital costs are reduced to $2.14 million and the operating cost is reduced to $0.11/kgal and $2.04/pulp-ton, or $0.054/kgal and $0.96/pulp-ton with water credit.

If minilime is used instead of microlime ahead of bio-oxidation (Estimate No. 6), the color would be 150 CU, if we assume there will be no color increase during bio-oxidation. (The two mills using minilime-bio-oxidation, Interstate Paper and Continental Can, have experienced large color increases during bio-oxidation of lime-treated water.) The capital costs (including that for bio-oxidation) for minilime-bio are 20% greater than for microlime-bio and the operating costs are 36% greater.

These comparisons indicate that microlime-bio has significantly lower capital and operating costs than minilime-bio but that the color of the water from microlime-bio will be greater and probably limit its suitability for reuse applications. These comparisons also indicate that, if water that has higher color (150 - 300 CU) but lower BOD concentrations (35-40 mg/l) can be reused in the mill, either microlime-bio or minilime-bio can provide the water at significantly lower capital and operating costs than microlime-carbon.

Microlime versus Minilime

The microlime and minilime processes without subsequent treatment steps are compared in Table 39 when treating effluent from an older mill (Estimates Nos. 9 and 11) and from a new mill (Estimates Nos. 8 and 10).

Before credit for reused water, the minilime process in both cases has a 57% greater capital cost and a 71% greater operating costs. In the older mill, microlime treatment would cost $1.82/pulp-ton compared to $3.11 for the minilime treatment. The microlime process has an additional advantage in that it could be operated when the lime kiln is off since the treated water does not require carbonation and the lime dosage is much smaller. These advantages are partially offset by some disadvantages: microlime provides treated water having 300 CU as compared to 150 CU for water from the minilime process, the TOC concentration is slightly greater, the control of lime addition to maintain the soluble calcium in a narrow range of about 70 to 90 mg/l is more demanding than maintaining a fixed dosage, and the greater hardness value of the product water (about 200 mg/l $CaCO_3$) might limit its use in some parts of the mill.

The combinations of microlime and minilime with carbon adsorption are compared in Estimates Nos. 1 and 7 for an older mill. The capital cost for microlime-carbon is 5% less and the total operating cost is 10% less ($0.50/pulp-ton), which gives microlime a slight economic margin when used in the combined sequence to give water meeting the selected standards for reuse.

Effect of Carbon Price on Treatment Costs

The price of carbon used in all estimates discussed thus far was $0.27 per pound, which was typical for bulk quantities of commercial granular carbons (January 1973). Lower-cost granular carbons are now available that have higher ash contents, and new sources of carbon, such as from the St. Regis process of producing granular carbon from a hydropyrolysis pulp-chemicals recovery process that is now being developed under an EPA grant (Part II of No. 12040 EJU), indicate that lower-cost carbons might be available in the future. To show the effect of carbon price,

Table 39. COMPARISON OF COSTS FOR MICROLIME AND MINILIME PROCESSES

Estimate No.	11	9	10	8	1	7
Pulp tons per day	800	800	800	800	800	800
Effluent, gal/ton	18,000	18,000	12,000	12,000	12,000	12,000
Effluent, mil. gal/day	14.4	14.4	9.6	9.6	9.6	9.6
Treatment	microlime	minilime	microlime	minilime	microlime -carbon	minilime -carbon
Product water quality						
Color, CU	300	150	300	150	100	100
TOC, mg/l	150	135	150	135	100	100
BOD, mg/l	225	187	225	187	150	117
Capital costs, $ million						
Lime trt. & pH adjust.	2.36	3.68	1.85	2.91	1.85	2.91
Carbon adsorption					4.90	4.20
Clarifier and bio-oxidation						
Total	2.36	3.68	1.85	2.91	6.75	7.11
Operating costs, $/kgal						
Fixed	0.050	0.079	0.059	0.093	0.217	0.228
Labor, o.h., util.	0.018	0.035	0.018	0.035	0.075	0.087
Lime and chemicals	0.033	0.059	0.033	0.059	0.033	0.059
Carbon, at $0.27/lb					0.034	0.026
Total operating cost	0.101	0.173	0.110	0.187	0.359	0.400
Operating cost, $/ton pulp	1.82	3.11	1.32	2.25	4.30	4.79
Operating costs with water credit[a]						
$/kgal	0.041	0.113	0.050	0.127	0.300	0.340
$/ton pulp	0.74	2.03	0.60	1.53	3.58	4.07

[a] With credit of $0.06/kgal for mill make-up water

it was assumed that carbon having the same properties as the $0.27/lb carbon would be available at $0.10/lb if produced and used on-site. The influence of this lower-priced carbon on the costs of lime-carbon and bio-carbon sequences is shown in Table 40.

For microlime-carbon and minilime-carbon plants (Estimates Nos. 1, 2 and 7), the lower price of carbon reduced the capital costs 6 - 9% and the operating costs by 8 - 12% before credit for the reused water and 9-15% after credit for reused water. In the case of the primary-bio-carbon plant (Estimate No. 4) the lower priced carbon reduced the capital costs by 12% and the operating costs by 21%. The greater influence of carbon price on costs for primary-bio-carbon was due to the much greater dosage and size of carbon adsorption units to remove the higher concentration of color after bio treatment.

CONCLUSIONS FROM THE COST ESTIMATES

1. The microlime-carbon sequence is the lowest cost process for meeting the product water quality standards of 100 CU and 100 mg/l TOC for mill reuse. The capital costs for treating 9.6 mgd from a new 800 ton/day mill are estimated to be $6.75 million, and the total operating costs are estimated to be $0.30/kgal and $3.58/pulp-ton with credit for the reused water.
2. Doubling the plant pulping capacity increases the capital cost by 67% and reduces the operating costs about 12% to $0.26/kgal and $3.13/pulp-ton with credit for water.
3. Microlime-carbon treatment for an older mill producing 50% more water per pulp-ton but having the same pulp capacity requires a 38% greater capital cost, and the operating costs are about the same per 1000 gal ($0.28/kgal) but the cost per pulp-ton was greater ($4.96), both after credits for the reused water.
4. A reduction in price of carbon from $0.27/lb to $0.10/lb reduces the capital cost for lime-carbon plants about 8%, and operating cost about 13%.
5. The capital and operating costs for primary-bio-carbon are 1.5 to 2 times those for microlime-or minilime-carbon, and the costs for primary-carbon sequence are about 15% greater than those for primary-bio-carbon sequence.
6. The minilime-carbon process has about 5% greater capital and 14% greater operating costs than the microlime-carbon process.
7. For reuse of water in a new 800 ton/day mill, for applications that can tolerate a color of 300 CU and a hardness of 200 mg/l $CaCO_3$, microlime treatment could be used at a capital cost of only $1.85 million and an operating cost of only $0.11/kgal or $1.32/pulp-ton, or $0.05/kgal and $0.60/pulp-ton after credit for the water. The costs for microlime treatment are about 40% below those for minilime alone before credit for the water.

Table 40. EFFECT OF CARBON PRICE ON TREATMENT COSTS

Estimate No.	1		2		4		7	
Pulp tons per day	800		1600		800		800	
Effluent, gal/ton	12,000		12,000		18,000		12,000	
Effluent, mil. gal/day	9.6		19.2		14.4		9.6	
Treatment	microlime-carbon		microlime-carbon		bio carbon		minilime-carbon	
Carbon price, $/lb	0.27	0.10	0.27	0.10	0.27	0.10	0.27	0.10
Capital costs, $ million								
Lime trt. & pH adjust.	1.85	1.85	2.90	2.90			2.91	2.91
Carbon adsorption	4.90	4.35	9.00	7.91	11.92	9.95	4.20	3.75
Clarifier & bio-oxid'n					5.09[a]	5.09[a]		
Total	6.75	6.20	11.90	10.81	17.01	15.04	7.11	6.66
Operating costs, $/kgal								
Fixed	0.217	0.199	0.191	0.173	0.364	0.322	0.228	0.214
Labor, o.h., util.	0.075	0.075	0.064	0.064	0.127	0.127	0.087	0.087
Lime and chemicals	0.033	0.033	0.033	0.033	0.003	0.003	0.059	0.059
Carbon	0.034	0.012	0.034	0.012	0.146	0.054	0.026	0.010
Total operating cost	0.359	0.319	0.322	0.282	0.640	0.506	0.400	0.370
With water credit[b]	0.299	0.259	0.262	0.222	0.580	0.446	0.340	0.310

[a] Including capital cost of bio-oxidation

[b] With credit of $0.06/kgal for mill make-up water

8. Microlime-bio and minilime-bio processes are significantly lower in capital costs and 33 to 50% lower in operating costs than microlime-carbon, but the color of the product water will be greater, particularly if a color increase during bio-oxidation occurs as it does in the two mills using lime-bio treatment.

SECTION XV

REFERENCES

1. Black, A. P., and Christman, R. F. "Characteristics of Colored Surface Waters", J. Am. Water Works Assoc. 55 (6):753(1963).

2. Black, A. P., and Christman, R. F. "Chemical Characteristics of Fulvic Acids", J. Am. Water Works Assoc. 55 (7):897(1963).

3. Berger, H. F. and Brown, R. I. "The Surface Reaction Method for Color Removal from Kraft Bleaching Effluents", Tappi 42 (3):245(1959).

4. Berger, H. F., and Smith, D. R.. "Waste Water Renovation", Tappi 51 (10):37A(1968).

5. Davis, C. L. Jr. "Tertiary Treatment of Kraft Mill Effluent Including Chemical Coagulation for Color Removal", Tappi 52 (11):2132(1969).

6. English, J. N., et al. "Removal of Organics from Waste Water by Activated Carbon", Water-1970, AIChE Symposium Series 67 (107):147 (1971).

7. Gould, M. "Lime-Based Process Helps Decolor Kraft Wastewater", Chem. Eng. 78 (3):55(1971).

8. Gould, M. "Color Removal from Kraft Mill Effluent by an Improved Lime Process", Tappi 56 (3):79(1973).

9. Masse, A. N. "Removal of Organics by Activated Carbon", presented at 156th National A.C.S. meeting (Sept. 1968).

10. McGlasson, W. G. Thibodeaux, L. J., and Berger, H. F., "Potential Uses of Activated Carbon for Wastewater Renovation", Tappi 49 (12): 521(1966).

11. McGlasson, W. G. "Treatment of Pulp Mill Effluents with Activated Carbon", NCASI Tech. Bull. 199(1967).

12. Miller, C.O.M., and Clump, C. W. "A Liquid Phase Adsorption Study of the Rate of Diffusion of Phenol from Aqueous Solution into Activated Carbon", AIChE Journal 16 (2):169(1969).

13. Morris, J. C., and Weber, W. J. "Adsorption of Biochemically Resistant Materials from Solution", U.S.P.H.S., AWTR-9(1964).

14. Spruill, E. L. "Color Removal and Sludge Recovery from Total Mill Effluent", Tappi 56 (4):98(1973).

15. Timpe, W. G., Lang, E. W., et al. "The Use of Activated Carbon for Water Renovation in Kraft Pulp and Paper Mills", presented at 7th TAPPI Water and Air Conf., Minneapolis (June 1970).

16. Weber, W. J., Hopkins, C. B., and Bloom, R. "Physicochemical Treatment of Wastewater", J. Water Pollution Control Federation 42 (1): 83(1970).

17. Cover, A. E., and Pieroni, L. J. "Appraisal of Granular Carbon Contacting", Report Numbers TWRC-11 and TWRC-12, FWPCA, U.S. Department of the Interior (May 1969).

18. Anon. "Color Removal from Kraft Pulping Effluents by Lime Additon", Interstate Paper Corp. for EPA, Final Report, Program #12040 ENC, Grant #WPRD 183-01-68 (Dec. 1971).

19. Anon. "Process Design Manual for Carbon Adsorption", EPA Technology Transfer (October 1973).

20. Bloom, R., et al. "New Technique Cuts Carbon Regeneration Costs", Enviro. Sci. and Tech. 3 (3):214(1969).

21. Berg, E. L., et al. "Thermal Reactivation of Spent Powdered Carbon Using Fluidized Bed and Transport Type Reactors", Chem. Eng. Prog. Symposium Series 67 (107):154(1970).

22. Herbet, A. J. "A Process for Removal of Color from Bleached Kraft Effluents Through Modification of the Chemical Recovery System", NCASI Tech. Bull. 157 (June 1962).

23. Anon. "Design Workshop for Water Pollution Control", Environmental Science Services (November 12, 1969).

24. Smith, R. "Cost of Conventional and Advanced Treatment of Wastewater", J. Water Pollution Control Federation 40 (9):1546(1968).

25. DiGregorio, D. "Cost of Wastewater Treatment Processes", TWRC-6, FWPCA, U.S. Department of the Interior (Dec. 1968).

26. Anon. "Cost of Clean Water IV-- Projected Wastewater Treatment Cost in the Organic Chemicals Industry", FWPCA, U.S. Department of the Interior (Jan. 1969).

27. Anon. "Cost of Clean Water III - Industrial Waste Profiles No. 3 - Paper Mills" FWQA Publication No. IWP-3, U.S. Department of the Interior (Nov. 1967).

28. Eckenfelder, W. W. "Economics of Waste Treatment", Chemical Engineering 67, (18):109(1969).

29. Page, J. S. "Estimator's Manual of Equipment and Installation Costs", Gulf Publishing Co., Houston, (1963).

30. Guthrie, K. M. "Capital Cost Estimating", Chemical Engineering 76 (6):114(1969).

31. Berger, H. E. "Development of an Effective Technology for Pulp and Bleaching Effluent Color Reduction", presented at NCASI Meeting (Feb. 1969).

32. Davies, D. S. "Activated Carbon Eliminates Organics", Chemical Engineering Progress 60 (12):46(1964).

33. Hager, D. G., and Rizzo, J. L. "A Chemical and Physical Wastewater Treatment Process", presented at AIChE Meeting, Atlanta (Feb. 1970).

34. Cooper, J. C., and Hager, D. G. "Water Reclamation with Activated Carbon, Chemical Engineering Progress 62 (10):85(1966).

35. Spruill, E. L. Private Communication Concerning Costs for Continental Can Co. Lime Treatment Plant (July 1973).

36. Amberg, H. R. "Water Pollution Control in Pulp and Paper Industry", Industrial Water Engineering 7 (11):26(1970).

37. Bishop, D. F., et al. "Physical-Chemical Treatment of Municipal Wastewater", J. Water Pollution Control Federation 44 (3):361(1972).

38. "Standard Methods for Examination of Water and Wastewater", 13th Edition, APHA, New York(1971).

39. Ganczarczyk, J. "Fate of Lignin in Kraft Effluent Activated Sludge Treatment", J. Water Pollution Control Federation 45 (9):1898(1973).

40. Timpe, W. G., Lange, E. W., and Miller, R. L. "Kraft Pulping Effluent Treatment and Reuse-State of the Art", EPA R2-73-164, Program 12040 EJU (Feb. 1973).

41. Timpe, W. G., and Lange, E. W. "Processes for Reducing the Organic Carbon Content of Water Contaminated with Organic Compounds by Continuous Counter Current Multistage Treatment with Activated Carbon", U.S. Patent 3,763,040 (October 2, 1973).

42. Allan, G. G., Mauranen, P., Neogi, A.N. "Fiber Surface Modification, Part IX, Removal of Phenolic Pollutants from Water by Oxydative Coupling to Lignocellulosic Substrates", *Paperi ja Puu* No. 6 (1971); see also "Pollution Abatement by Fiber Modification", *EPA Final Report*, Program 12040-EFC (Jan. 1971).

43. Swanson, J. W., Dugal, H. S., *et al*. "Kraft Effluent Color Characterization Before and After Lime Treatment", *EPA R2-73-141*, Project 12040 DKD (Feb. 1973).

44. Culp, R. L., Culp, G. L. "Advanced Wastewater Treatment", Van Nostrand Reinhold Co., New York, p.253(1971).

45. Timpe, W. G., and Lang, E. W. "Activated Carbon Treatment of Kraft Mill Effluent for Reuse", Water-1973, *AIChE Symposium Series* 70(136): 579(1974).

46. Timpe, W. G., and Lang, E. W. "Activated Carbon and Other Techniques for Color Removal from Kraft Mill Effluents", Procedings of the XV EUCEPA Conference, Rome, ATICELCA in coop. w. FAO, Rome, p.535(1973).

47. Timpe, W. G., and Lang, E. W. "Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse-Pilot Plant Results", presented at TAPPI Environmental Conference (May 1973).

48. Thibodeaux, L. J., and Berger, H. F. "Laboratory and Pilot Plant Studies of Water Reclamation", *NCASI Tech. Bull*. *203* (June 19[illegible]).

49. Schoeffel, E. W., and Zimmermann, F. J. "Wet Air Oxidation of Combustible Materials Adsorbed on Carbonaceous Adsorbent", U.S. Patent 3,386,922 (June 4, 1968).

50. Koches, C. F. "Transport Reactor with a Venturi Tube Connection to a Combustion Chamber for Producing Activated Carbon", U.S. Patent 3,647,716 (March 7, 1972).

51. Koches, C. F., and Smith, S. B. "Reactivate Powdered Carbon", *Chem. Eng*. *79* (9):46(1972).

52. Bennett, D. J., Dence, C. W., *et al*. "The Mechanism of Color Removal in the Treatment of Spent Liquors with Lime", *TAPPI* *54* (12):2019(1971).

SECTION XVI

PUBLICATIONS AND PATENTS

PUBLICATIONS AND PAPERS PRESENTED

Timpe, W. G., Lang, E. W., *et al.*, "The Use of Activated Carbon for Water Renovation in Kraft Pulp and Paper Mills", presented at 7th TAPPI Water and Air Conf., Minneapolis (June 1970).

Timpe, W. G., "Removal of Color from Kraft Mill Effluents by Activated Carbon and Combined Treatments", presented at the NCASI Southern-South Central Regional Meeting, Atlanta, Ga., (July 1970).

Timpe, W. G., and Lang, E. W., "The Removal of Color from Kraft Mill Effluents by Activated Carbon and Combined Treatments", presented at the 1971 Annual Meeting, Gulf Coast Section, TAPPI, Biloxi, Miss. (May 1971).

Timpe, W. G., "A Chemical Engineering Approach to a Closed Water Cycle in the Kraft Industry", presented at the Ninth API - TAPPI Research Conference, Seattle, Wash., (Oct. 1971) (presented by G. R. Webster of EPA).

Timpe, W. G., Lang, E. W., and Miller, R. L., "Kraft Pulping Effluent Treatment and Reuse-State of the Art". *EPA R2-73-164*, Program 12040 EJU (Feb. 1973).

Timpe, W. G., and Lang, E. W., "Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse-Pilot Plant Results", presented at TAPPI Environmental Conference (May 1973).

Timpe, W. G., and Lang, E. W., "Activated Carbon and Other Techniques for Color Removal from Kraft Mill Effluents", Procedings of the XV EUCEPA Conference, Rome ATICELCA in coop. w. FAO, Rome, p.535(1973).

Timpe, W. G., and Lang, E. W., "Activated Carbon Treatment of Kraft Mill Effluent for Reuse", *Water-1973, AIChE Symposium Series* *70*(136):579(1974).

PATENTS AND PATENTS APPLIED

Timpe, W. G., and Lang, E. W., "Processes for Reducing the Organic Carbon Content of Water Contaminated with Organic Compounds by Continuous Counter Current Multi-stage Treatment with Activated Carbon", U.S. Patent 3,763,040 (October 2, 1973) (This is the so-called FACET process).

Timpe, W. G., "Process for Reducing the Organic Carbon Content and Improving the Color of Aqueous Plant Effluents", U.S. Patent Application Serial No. 301,400 (Nov. 1, 1972).

Timpe, W. G., "Separation of Organic Compounds in Aqueous Condensates from Kraft Pulping", U.S. Patent Application Serial No. 301,401 (Nov. 1, 1972).

SECTION XVII

GLOSSARY

BOD - 5-day biological oxygen demand.

CU - Color units measured according to APHA-NCASI standard method (see Appendix B).

FPCU - Color after filtration through 2 micron paper filter, no pH adjustment (see Appendix B).

MPCU - Color after filtration through 0.8 micron Millipore filter, no pH adjustment (see Appendix B).

TIC - Total inorganic carbon.

TOC - Total organic carbon.

Lime treatment - Effluent treatment based on the use of lime - see minilime and microlime treatment.

Lime-carbon
Primary/lime-carbon - Terms used interchangeably for an effluent treatment system involving lime treatment without prior or separate primary clarification followed by carbon adsorption.

Minilime treatment - Effluent treatment with the minimum lime dose that reaches near-leveling off of color at about 85% removal; dosage approx. 1000 mg/l CaO, leaving about 400 mg/l dissolved Ca in solution which must then be removed by carbonation (see Section VIII).

Microlime treatment - Effluent treatment achieving about 70% color removal; dosage adjusted to achieve 80 mg/l dissolved Ca, avoiding need for subsequent removal of Ca by carbonation; dosage approx. 500 mg/l CaO (see Section VIII).

Primary-carbon - Effluent treatment sequence involving primary clarification followed by activated carbon adsorption.

Bio-carbon
Primary-bio-carbon - Terms used interchangeably for an effluent treatment system involving primary clarification, biological oxidation and carbon adsorption.

Adsorption isotherm - Relates the quantity adsorbed per unit of adsorbent to the concentration of adsorbate at equilibrium.

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APPENDIX A

WATER QUALITY STANDARDS FOR SPECIFIC USES

The objective of maximizing water reuse economically very likely will require avoidance of non-essential treatment by more closely matching treated water quality to actual use requirements.

At present, no comprehensive listing appears to be available on water quality standards for specific water uses throughout the pulp and paper mill. Although certain standard use and reuse patterns exist throughout the industry, no standards have been developed for the water input for many individual process steps. A substantial amount of reuse is at present handled to fit specific mill circumstances, and disagreement is found as to what represents suitable water. The situation is made more complex by the fact that certain contaminant levels cannot be defined in terms of concentration in the water feed stream alone. If the receiving system is a water recycling system, consideration of maximum concentration in the receiving recycle system together with the feed and blowdown volumes is required. In other cases, a system downstream must be considered together with the direct receiving system. Temperature requirements must also be considered.

A beginning was made in October, 1969, to collect quality standards data and guidelines, resulting in the data in Table 41 and notes to this table.

Table 41. POTENTIAL WATER QUALITY STANDARDS FOR SPECIFIC WATER USES

USE	Flow, gal/ton pulp	STANDARD												
		Temp. °F	BOD mg/l	Organics mg/l	Color CU	Turbid. JTU	Total solids mg/l	Susp. solids mg/l	Diss. solids ug/l	pH	Hardness mg/l	Cl^- mg/l	$SO_4^=$ mg/l	Na^+ mg/l
Paper machine														
Headbox & wire showers low volume, high pressure, make-up		135(board)3)* 103(paper)	2-5 4)	3, 4)	50-100	10-15	<250 5)	0-5 6)	5)	2)	7)		2000 1,2)	
Felt showers			2-5		50-100	10-15				6-10 8)	7)	250	250	
Pulp mill														
Brown stock washer) fresh showers	1250-1500	160		12)	100 10)			fiber-free	9)	11)	9)			
last drum) contam.showers	1250-1500	160	13)	13)	13)				9)	11)	9)			
White liquor system														
White liquor filter (Eimco System)	100-200	125-200		21)	50-100					16)				14)
Mud washer		125-200		21)	50-100					16)				15)
Smolt dissolving 23)				21)	50-100							22)		
Bleaching system														
Fresh water in counter-current system 19)		19)			0-10					6-9	No Ca			
Woodyard 17)														
Showers	0-2000gpm 30)	<105 18)								6 or higher 18)				
Cooling and sealing water 20)														
Boiler feed water														
Cooling water														
Turbine and evaporator 24)		<95												
Small heat exch.; seal water on 26) pumps, bearings; air cond.; air compr.				26)	<50	5		25)			24)			.2-.5

* See notes at end of table

Notes to Table 41. WATER QUALITY STANDARDS FOR SPECIFIC WATER USES

1. Corrosion is problem.
2. 2000 ppm of SO_4= in white water is probably the TAPPI established limit in conjunction with wet strength resin use. Concentration in total white water, hence level in this make-up stream, is function of make-up flow and SO_4= (incoming with pulp and $Al_2(SO_4)_3$ and H_2SO_4 added for pH adjustment.
3. Refining adds 5°F.
4. No rosins or resins should be present to avoid plugging up machine showers; also, keep slime down by slimicides and residual Cl_2 of 0.2 mg/l (this is done anyway).
5. Watch in conjunction with chloride and sulfate build-up.
6. Related to turbidity specification.
7. Possibly need a Ca spec., a minimum being required for proper functioning of sizing or wet strength additives; 40-50 ppm Ca suggested. $Ca(HCO_3)_2$ hardness undesirable.
8. Adjust to maintain stability of water.
9. Water must be free of contaminants which would form scale in heat exchanger or deposit on filter/washer wires. Low Ca and Fe desired.
10. Lower limits apply if pulp is to be bleached.
11. Probably 7-12. Essential to avoid lignin precipitation at this point.
12. Low molecular weight organics pose no direct problems except as nutrients in paper machine water system, resulting in slime growth. Could be high as "contaminated condensate" without carry-over (i.e., clean evaporator condensate).
13. Can be contaminated up to perhaps 1% BLS. There is a concentration of about 2% to 4% BLS in collection system under drum. Firmer data need to be established through tests and calculations.
14. A low Na content is desired. A certain Na limit may be calculated from washing requirements: washing done on 12% Na in liquid; 0.5% to 2.0% Na desired in dry mud, at 60% to 70% solids in cake.
15. Since this is the final washing stage for the lime mud, low Na content in wash water may be even more critical than as discussed in note 14.
16. Low pH acceptable if alkali consumption can be limited.
17. Only concern is to avoid excessive foaming. Otherwise, a closed recycle system is now contemplated for Mill B.
18. Uncertain. Consider effect of higher temperatures on extraction of wood acids and on CO_2 absorption from air. Corrosion due to low pH is to be avoided.
19. Consider that there are three water systems to a bleach plant (batch):
    a. Cold or ambient temperature water
    b. 115°F water
    c. 160°F water
20. In Mill A water is first used as cooling water before other uses.
21. Presence of low molecular weight organics considered not presenting a problem.

22. As low as possible. Chloride build-up in liquor system to be avoided.
23. Use of weak wash water is standard. Contaminated condensate (such as clean evaporator condensate) can be used.
24. Relatively clear water, stabilized, non corrosive, non scaling.
25. Either no suspended solids, or otherwise chemically controllable.
26. Stabilized, non corrosive, non scale forming, non slime forming.

APPENDIX B

PROCEDURES FOR ISOTHERMS, LABORATORY LIME TREATMENT, LABORATORY BIO-OXIDATION AND ANALYSES

PROCEDURE FOR MAKING CARBON ADSORPTION ISOTHERMS(44)

1. Pulverize a representative sample of the carbon (10-20g) and screen it through a 325-mesh sieve. Oven-dry the carbon for 3 hr at 150°C.
2. Obtain a representive sample of the wastewater to be tested, making sure that the pH is that of the original source of the sample. In the laboratory program (Section 4), samples were adjusted to the average pH for a given stream if the samples were within 0.7 pH units of the average, or not used if outside of this range.
3. Weigh out 5 amounts of carbon in disposable weighing dishes. For pulp mill effluents, use 0.3, 0.5, 1.0, 2.5, and 5.0 g per 500 ml of sample (0.6 - 10.0 g/1).
4. Add 500 ml of the water to be tested to a 1-liter beaker, heat to 40°C, add one of the weighed dosages of carbon, stir vigorously (100 rpm on a Phipps and Bird gang-stirrer) for 15 minutes while maintaining the water at 40°C. Filter about 100 ml of the water through Whatman No. 2 filter paper using a pressure-type lab filter (to prevent loss of volatile organics). (Isotherms, except those on condensate streams, prepared prior to 6/71 were made at 95°C and 2 minutes, but were equivalent to those made at 40° and 15 minutes.)
5. Repeat for the other dosages of carbon with separate 500-ml quantities of water to be tested.
6. Analyze the filtrate from each dosage of carbon for the impurity of interest and express in mg/l or APHA color units. Normally, isotherms were prepared for both TOC and color.
7. For each carbon dosage, subtract the final from the initial impurity concentration, and divide this difference by the dosage of carbon in g/l. This number is the loading of impurity per g of carbon used. On 3 x 3 cycle log-log graph paper, plot loading on the y-axis versus remaining concentration on the x-axis. The isotherm is completed by drawing a straight line through the plotted values. (Sometimes the line has two slopes and has a dog-leg shape.) Extrapolate the line to the initial concentration. The loading at this intercept is the ultimate capacity of the carbon for that effluent.

LABORATORY BIO-OXIDATION

Bio-oxidation was standardized so that approximately a 70% reduction in BOD would be obtained. The following conditions were used: Aeration for 40 hours with filtered air; ammonium nitrate addition of 3 mg/l per 100 mg/l BOD in the feed; phosporic acid addition of 0.6 mg/l per 100 mg/l BOD; strained sewage addition of 25 mg/l per 100 mg/l BOD.

LABORATORY LIME TREATMENT

The standard laboratory lime treatment consists of lime addition, separation of precipitate, carbonation to pH 10.5 to remove excess dissolved lime, separation of precipiate, and finally carbonation to pH 7.0. A lime dosage of 5000 mg/l CaO was used unless otherwise specified. This is a compromise dosage and is well above the so-called minimum lime (minilime) dosage of 1-2,000 mg/l (5,14) (also called stoichiometric), but below the so-called massive lime dosage of 20,000 mg/l (22). The lime dosage was slaked in 500 ml of effluent for treatment of 6-10 liter of effluent. The slurry was poured into the effluent and mixed in a 5 gal tank. The mixture was held under slow stirring for 5 minutes. The mixture was allowed to settle and the supernatant was then filtered through a Whatman No. 2 filter. The filtrate was placed into another tank and bottled CO_2 was bubbled into the sample using a gas dispersion tube. The sample was slowly stirred during carbonation which continued until the pH reached 10.5. The slurry was again allowed to settle and the supernatant was filtered through a Whatman No. 2 filter. Carbonation was then continued down to a pH of 7.0. This treatment follows the NCASI procedure (22).

LABORATORY PRIMARY CLARIFICATION

All samples were filtered through a Whatman No. 2 paper filter to simulate the result of primary clarification.

ANALYTICAL METHODS

The methods used for analyses of samples in the work covered by this report are listed below. The standard method number given refers to the method in the 13th edition of Standard Methods (38). Methods modified by St. Regis Paper Company are available on request.

Color - Std Method 206A in which the pH of the sample is adjusted to 7.6 and the sample filtered through a 0.8 micron Millipore filter and light transmittance is measured at 465 nm on a Spectronic 70 spectrophotometer, as adopted by the NCASI. Prior to 2/4/71, the NCASI adopted method called for filtration through 0.45 instead of 0.8 micron Millipore filter, and light transmittance measurement at 430 nm instead of 465 nm. In both cases, color is determined from a calibration curve using a cobalt chloroplatinate standard, where equivalent mg/l of cobalt chloroplatinate is termed color units or "CU". Based on pilot plant experience, it was found desirable to determine the parameter of "color" not only by the industry standard APHA-NCASI method but also by modified procedures which measure apparent color. One modified procedure involved 0.8 micron Millipore filtration prior to adjustment to pH 7.6. (Used after lime treatment, this procedure ensures more complete removal of suspended solids.) Another modified procedure consisted of measuring color after filtration through a Whatman No. 2 filter paper and adjustment to pH 7.6, referred to as "7.6 FPCU". A third modified procedure consisted of measuring color after filtration through Whatman No. 2 filter paper without pH adjustment, noted as "FPCU". A fourth modified procedure consisted of measuring color after filtration through an 0.8 micron Millipore filter without any pH adjustment, noted as "MPCU".

TOC and TIC - Std Method 138 using a Beckman 915 total carbon analyzer; sample filtered through Whatman No. 2 paper filter.

pH - Std Method 144A

Turbidity - Std Method 163A using a Hach Model 2100 turbidimeter.

Total Suspended Solids (TSS) - Std Method 224C using Whatman GF/C glass fiber filter discs.

Conductivity - Std Method 154 using Yellow Springs Instrument Co. Model 31 conductivity bridge.

BOD-5 - Std Method 219

Dissolved Oxygen (DO) - Std Method 218F using a Weston and Stack dissolved oxygen analyzer Model 300.

Na_2S - Mercuric chloride titration method according to E. Bilberg, Norsk Skogindustri, 11/58 470 (1958), modified by St. Regis Paper Company.

Na_2S_x and $Na_2S_2O_3$ - by unpublished methods developed by St. Regis Paper Co.

Sulfate - Std Method 156B, gravimetric method.

Chloride - Orion Instrument Company selective ion electrode method.

Metal ions - Std Method 129A using atomic adsorption with the Perkin-Elmer Model 403 spectrophotometer.

Volatile Acids - by gas chromatographic method of S. M. Aronovic, *et al*, TAPPI 54 1963 (1971) and modified by St. Regis Paper Company.

Neutral Volatiles - by gas chromatographic method of B. G. Turner and I. T. Van Horn, presented at TAPPI National Meeting, February 1970, and modified by St. Regis Paper Company.

APPENDIX C

DETAILED INFORMATION ON PILOT PLANT EQUIPMENT

1. Basin volume - 25,000 ft^3 or 187,000 gal, retention time at 30 gpm = 4.3 days
    - aerator - 5 hp Chemineer
    - clarifier - area 510 ft^2, rise rate at 30 gpm = 86 gpd/ft^2 = 0.06 gpm/ft^2

2. Surge tank, 10,000 gal, for backwash water (normally) or surge capacity between stages of processing

3. Lime treatment - by Potter and Rayfield
    - lime treater, dimensions - 10'd x 11'-6"h, 4900 gal.
        - rise rate at 30 gpm = 550 gpd/ft^2 = 0.38 gpm/ft^2
        - retention time in mixing zone - 20 min.
        - retention time total = 2.7 hr.
        - lime feed rate for 30 gpm and 1300 mg $Ca(OH)_2$/l = 20/lb hr.
        - lime feeder - Wallace and Tiernan Series A-728 volumetric feeder with 41 ft^3 hopper and 50 gal mixing tank for lime slurry.
    - carbonator, dimensions - 7'-6"d x 11'-6"h, 2920 gal, rise rate at 30 gpm = 980 gpd/ft^2 = 0.68 gpm/ft^2
        - CO_2 from cylinders, pH automatically controlled (normally at 10.5)
    - pH adjust tank, 200 gal, CO_2 through controller to reduce pH to about 8.5

4. Carbon columns - by Potter and Rayfield
    - four columns piped to permit any combination of series and parallel flow up-flow or down-flow.
    - dimensions - 3'd x 15'h, 430 gal in bed, 795 gal total
    - carbon bed - 10' supported on sand-gravel plus 5' free-board at top.
    - charge - 1600 lb ICI America (Atlas Chemical) granular Darco 20 x 40 mesh.
    - retention time in bed at 15 gpm = 0.6 hr = 2.4 hr total.
    - flow vel. at 15 gpm = 2 gpm/ft^2 = 1.7 bed volumes/hr each col.
    - backwash = 30 gpm, normally every 48 hr, after air backwash.
    - carbon density = 25 lb/ft^3.

5. FACET, three stirred tanks, gravity flow of water, carbon slurry pumped counter-current to water flow, with sloping baffle to provide settling zone at top of tank.

5. FACET (continued)

3'd x 5'h (straight side) 170 gal in mixing zone, 248 gal total
retention time in mixing zone at 10 gpm=17 min ea = 51 min total
at 15 gpm=11 min ea = 33 min total
rise rate at 10 gpm=1.4 gpm/ft^2
at 15 gpm=2.1 gpm/ft^2
weight of carbon in each tank at 10% solids = 170 lb.
operating densities = 10-20% in mixing zone.
Carbon - ICI America, Darco XPT 40 x 140 mesh.
carbon feeder - Wallace and Tiernan, Series A-728 volumetric feeder and 90 ft^3 hopper.

6. Duo-media filters - by Potter and Rayfield

before carbon columns -
4'd, 12.5 ft^2 area, 1' of 0.4 x 0.6mm sand plus 1' of 1 x 3 mm anthracite, flow velocity = 2.1 gpm/ft^2 at 15 gpm.
after FACET -
3'd, 7.05 ft^2, 1' of sand plus 1' of anthracite, flow velocity = 2.1 gpm/ft^2 at 15 gpm.

7. Instrumentation - by Foxboro

recorders -

a. 10 temperatures
b. pH of controlled streams - carbonator and pH adjust
flow rates - to lime system, to carbon columns, and to FACET
c. measured properties of sample streams = pH, color, turbidity, conductivity. 12 sample streams that can be monitored instrumentally, Tenor drum programmer switches flow of sample stream to measurement sensors and controls recording of properties on recorder.

Controlled parameters = 3 water flow rates and 2 pH values (carbonator and pH adjust).
timer controlled blow-down of sludge from lime treater and carbonator.

8. Parameters determined in lab analyses of samples from carbon treatments - color, pH, total inorganic carbon, total organic carbon, soluble calcium (at least daily).
volatiles and low molecular weight organics, suspended solids, BOD (every few days).

APPENDIX D
PRINTOUT OF DAILY SUMMARIES OF CONDITIONS AND RESULTS FOR BIO-CARBON SEQUENCE

```
DATE=08/15/72  TIME=16:26: 8

RR012 - WATER TREATMENT PILOT PLANT FILE DUMP
DATE              |   11FB                               |   13FB                               |   14FB                               |   15FB
TIME OF DAY       |   0800                               |   0800                               |   0800                               |   0800
COLUMN NAME       |      D        C        A        B    |      D        C        A        B    |      D        C        A        B    |      D        C        A        B
HRS OPERATED      |   21.50    21.50    21.50    71.50   |   46.00    46.00    46.00    46.00   |   23.00    23.30    23.00    23.30   |   22.25    22.25    22.25    22.25
FLOW RATE GPM     |   15.00     0.0      0.0      0.0    |   15.00     0.0      0.0      0.0    |   14.00     0.0      0.0      0.0    |   15.00     0.0      0.0      0.0
TEMP BASIN F      |  105.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  138.00     0.0      0.0      0.0
TEMP COLUMN F     |   74.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |   70.00     0.0      0.0      0.0
CU TO BASIN  PAPR | 2045.48     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  565.72     0.0      0.0      0.0    | 1090.24     0.0      0.0      0.0
 (CU/L)        MP | 1765.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  510.00     0.0      0.0      0.0    |  900.00     0.0      0.0      0.0
CU FM BASIN  PAPR |  910.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  825.00     0.0      0.0      0.0    |  825.00     0.0      0.0      0.0
               MP |  750.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  565.00     0.0      0.0      0.0    |  600.00     0.0      0.0      0.0
CU PORT-0    PAPR |1150.001000.00   750.00   585.00    | 1165.00   825.00   675.00   540.00   |  845.00   675.00   525.00   450.00   |  825.00   640.00   480.00   465.00
               MP |  825.00   570.00   338.00   233.00 |  715.00   525.00   345.00   259.00   |  620.00   450.00   265.00   225.00   |  640.00   435.00   285.00   210.00
CU PORT-2    PAPR |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
               MP |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
CU PORT-5    PAPR | 1000.00   750.00   585.00   435.00   |  825.00   675.00   540.00   426.00   |  675.00   525.00   450.00   390.00   |  640.00   480.00   465.00   383.00
               MP |  570.00   338.00   233.00   141.00   |  525.00   345.00   259.00   180.00   |  450.00   285.00   225.00   173.00   |  435.00   285.00   210.00   173.00
TOC TO BASN  MG/L |  351.48     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  116.72     0.0      0.0      0.0    |  187.24     0.0      0.0      0.0
TOC FM BASIN      |  126.00     0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |   92.00     0.0      0.0      0.0    |  101.00     0.0      0.0      0.0
TOC PORT-0        |  151.00    99.00    84.00    68.00   |  119.00    85.00    60.00    53.00   |   99.00    65.00    50.00    30.00   |  105.00    72.00    55.00    50.00
TOC PORT-2        |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
TOC PORT-5        |   99.00    84.00    68.00    57.00   |   85.00    60.00    53.00    43.00   |   65.00    50.00    30.00    35.00   |   72.00    55.00    50.00    42.00
BOD TO BASN  MG/L |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |  126.00     0.0      0.0      0.0
BOD FM BASIN      |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |   49.00     0.0      0.0      0.0
BOD FM LAST CCL   |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
DO FM BASIN  MG/L |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
PH TO COLUMNS     |    8.40     0.0      0.0      0.0    |    7.80     0.0      0.0      0.0    |    8.10     0.0      0.0      0.0    |    8.00     0.0      0.0      0.0
PH FM COLUMNS     |    8.40     8.30     8.30     8.30   |    7.90     7.80     7.70     7.80   |    7.90     7.90     7.92     8.00   |    7.93     8.30     7.90     8.20
COND MICRO MHOS   |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
TURB JTU TO BASN  |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
         FM BASN  |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
PRESS DROP COLS   |    7.00     2.00     5.02     0.0    |   12.02     2.00     3.00     0.0    |    4.00     2.02     3.00     0.0    |    3.00     2.00     2.02     0.0
PRESS DROP F-1    |   37.08     0.0      0.0      0.0    |   18.10     0.0      0.0      0.0    |   30.09     0.0      0.0      0.0    |   37.09     0.0      0.0      0.0
CHARGE LB         |1600.001600.001600.001760.00        |1600.001600.001600.001760.00        |1600.001600.001600.001760.00        |1600.001600.001600.001760.00
CUM HRS OPTD      |  417.50   345.50   188.50    38.50   |  463.50   391.50   234.50    84.50   |  486.50   414.50   257.50   107.50   |  508.75   436.75   279.75   129.75
CUM FLOW MGAL     |  375.79   310.27   167.92    34.65   |  417.19   351.67   209.32    76.05   |  436.51   370.99   228.64    95.37   |  456.56   391.02   248.67   115.39
COLOR LDG CU/G    |   25.75    23.43    10.60     8.45   |   41.05    38.89    18.58    15.52   |   17.14    16.64     6.05     4.77   |   21.42    15.68     7.84     3.32
CUM COLOR LDG     |  479.54   232.85   113.84    20.21   |  520.59   271.74   132.42    35.72   |  537.73   288.38   138.47    40.49   |  559.16   304.05   146.31    44.00
COLOR LDG RATE    |    1.20     1.09     0.49     0.39   |    0.89     0.85     0.40     0.34   |    0.75     0.72     0.26     0.21   |    0.96     0.70     0.35     0.16
TOC LDG MG/G      |    5.25     1.51     1.62     1.01   |    7.35     5.40     1.51     1.96   |    3.43     1.51     2.02    -0.46   |    3.45     1.78     3.52     0.76
CUM TOC LDG       |   63.82    29.05    12.84     2.90   |   71.16    34.45    14.35     4.86   |   74.59    35.96    16.37     4.40   |   78.04    37.74    16.89     5.16
TOC LDG RATE /HR  |    0.24     0.07     0.08     0.05   |    0.16     0.12     0.03     0.04   |    0.15     0.07     0.09    -0.02   |    0.15     0.08     0.02     0.03
COLOR REMOVAL %   |   30.91    40.70    31.07    39.48   |   26.57    34.29    24.93    30.50   |   27.42    36.67    21.05    23.11   |   32.03    34.48    26.32    17.62
TOTAL REMOVAL %   |   82.91     0.0      0.0      0.0    |   74.83     0.0      0.0      0.0    |   72.10     0.0      0.0      0.0    |   72.97     0.0      0.0      0.0
TOC REMOVAL %     |   34.44    15.15    19.05    16.18   |   28.57    29.41    11.67    18.67   |   34.34    23.08    40.00   -16.67   |   31.43    23.61     9.09    16.00
TOTAL REMOVAL %   |   62.25     0.0      0.0      0.0    |   63.87     0.0      0.0      0.0    |   64.65     0.0      0.0      0.0    |   60.00     0.0      0.0      0.0
BOD REMOV BASN %  |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |   61.11     0.0      0.0      0.0
BOD REMOV COLS %  |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0    |    0.0      0.0      0.0      0.0
COLOR REM % SYST  |   30.91    28.12    12.73    11.15   |   26.57    25.17    12.03    11.05   |   27.42    26.61     9.68     8.39   |   32.03    23.44    11.72     5.78
TOC REM % SYS IN  |   34.44     9.93    10.60     7.28   |   28.57    21.01     5.88     8.40   |   34.34    15.15    20.20    -5.05   |   31.43    16.19     4.76     7.62
COLOR % OF FEED   |   69.09    40.97    28.24    17.09   |   73.43    48.25    36.22    25.17   |   72.58    45.97    36.29    27.90   |   67.97    44.53    32.81    27.03
TOC % OF FEED     |   65.56    55.63    45.03    37.75   |   71.43    50.42    44.54    36.13   |   65.66    50.51    30.30    35.35   |   68.57    52.38    47.62    40.00
OPERATING DAY #   |   57.00     0.0      0.0      0.0    |   59.00     0.0      0.0      0.0    |   60.00     0.0      0.0      0.0    |   61.00     0.0      0.0      0.0
COLOR RATE TOT*C  |   71.91    71.91    71.91    71.91   |  120.34   120.34   120.34   120.34   |   46.92    46.92    46.92    46.92   |   50.81    50.81    50.81    50.81
TOC LDG RATE T*C  |    9.88     9.88     9.88     9.88   |   17.10    17.10    17.10    17.10   |    6.72     6.72     6.72     6.72   |    6.85     6.85     6.85     6.85

DISK FILE LOCN        145      146      147      148        149      150      151      152        153      154      155      156        157      158      159      160
```

APPENDIX E
PRINTOUT OF DAILY SUMMARIES OF CONDITIONS AND RESULTS FOR PRIMARY-CARBON SEQUENCE

```
DATE=12/10/72  TIME= 7:59:51

RR012 - WATER TREATMENT PILOT PLANT FILE DUMP
DATE                   05MY                              06MY                              07MY                              08MY
TIME OF DAY            0800                              0830                              1400                              0800
COLUMN NAME                C        A        B        D        A        B        D        C        A        B        D        C        A        B        D        C
HRS OPERATED           23.00    23.00    23.00    23.00    24.50    24.50    24.50    24.50    29.50    29.50    29.50    29.50    16.00    16.00    16.00    16.00
FLOW RATE GPM          10.00      0.0      0.0      0.0    10.00      0.0      0.0      0.0    10.00      0.0      0.0      0.0    10.00      0.0      0.0      0.0
TEMP BASIN F          114.00      0.0      0.0      0.0   106.00      0.0      0.0      0.0   110.00      0.0      0.0      0.0   115.00      0.0      0.0      0.0
TEMP COLUMN F          80.00      0.0      0.0      0.0    70.00      0.0      0.0      0.0    76.00      0.0      0.0      0.0    82.00      0.0      0.0      0.0
CU TO BASIN PAPR         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
  (CU/L)      MP         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
CU FM BASIN PAPR     1425.00      0.0      0.0      0.0  1650.00      0.0      0.0      0.0  1465.00      0.0      0.0      0.0  1425.00      0.0      0.0      0.0
              MP     1125.00      0.0      0.0      0.0  1200.00      0.0      0.0      0.0  1125.00      0.0      0.0      0.0   975.00      0.0      0.0      0.0
CU PORT-0     PAPR   1425.00   750.00   947.00   413.00  1650.00   750.00   458.00   428.00  1350.00   600.00   450.00   405.00  1383.00  1125.00   450.00   408.00
              MP     1125.00   600.00   525.00   293.00  1350.00   600.00   345.00   300.00  1125.00   570.00   330.00   293.00  1050.00   525.00   338.00   300.00
CU PORT-2     PAPR       0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
              MP         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
CU PORT-5     PAPR    750.00   947.00   413.00   383.00   750.00   458.00   428.00   210.00   600.00   450.00   405.00   315.00  1125.00   450.00   408.00   360.00
              MP      600.00   525.00   293.00   255.00   600.00   345.00   300.00   105.00   570.00   330.00   293.00   218.00   525.00   338.00   300.00   203.00
TOC TO BASN MG/L         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
TOC FM BASIN          191.00      0.0      0.0      0.0   228.00      0.0      0.0      0.0   228.00      0.0      0.0      0.0   217.00      0.0      0.0      0.0
TOC PORT-0            198.00   123.00    97.00    96.00   233.00   125.00   116.00    82.00   232.00   104.00   109.00    88.00   221.00   137.00   121.00   105.00
TOC PORT-2               0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
TOC PORT-5            123.00    97.00    96.00    70.00   125.00   116.00    82.00    72.00   104.00   109.00    88.00    70.00   137.00   121.00   105.00    88.00
BOD TO BASN MG/L         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
BOD FM BASIN             0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
BOD FM LAST COL          0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
DO FM BASIN MG/L         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
PH TO COLUMNS          10.30      0.0      0.0      0.0    10.50      0.0      0.0      0.0    10.20      0.0      0.0      0.0    10.20      0.0      0.0      0.0
PH FM COLUMNS          10.10    10.00 [illegible]  9.80    10.20    10.10     9.50     9.50    10.30    10.20     9.80     9.10    10.10    10.10    10.00     9.00
COND MICRO MHOS        50.00    50.00    50.00    50.00    50.00    50.00    50.00    50.00      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
TURB JTU TO BASN       20.00      0.0      0.0      0.0    22.00      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
         FM BASN       16.00    14.00    14.00    14.00    15.00    15.00    15.00    15.00      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
PRESS DROP COLS         1.00     1.00     1.00     1.01     1.01     1.01     1.00     1.00     1.00     1.00     1.01     1.01     1.01     1.01     1.00     1.00
PRESS DROP F-1          1.01      0.0      0.0      0.0     1.01      0.0      0.0      0.0     1.01      0.0      0.0      0.0     1.01      0.0      0.0      0.0
CHARGE LB            1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00  1600.00
CUM HRS OPTD          527.25   388.25   250.75    92.00   412.75   275.25   116.50    24.50   442.25   304.75   146.00    54.00   458.25   320.75   162.00    70.00
CUM FLOW MGAL         329.62   232.95   150.45 [illegible] [illegible] [illegible] 69.90 14.70  265.35   182.85    87.60    32.40   275.95   192.45    97.20    42.00
COLOR LOG CU/G         37.81     5.45    16.71     2.74    57.58    19.56     3.45    14.96    51.27    22.17 [illegible] [illegible] 26.30   9.37     1.90 [illegible]
CUM COLOR LOG         391.14 [illegible] 89.27    23.05   234.75    99.83    26.50    14.96   286.02   122.00    29.92    21.89   312.32   131.37 [illegible] [illegible]
COLOR LOG RATE     [illegible] [illegible] [illegible] 0.12 2.35   0.80     0.14     0.61     1.74     0.75     0.12     0.23 [illegible] [illegible] [illegible] [illegible]
TOC LOG MG/G       [illegible] [illegible] [illegible] 1.15 [illegible] 0.69 [illegible] 0.77 [illegible] -0.46 [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
CUM TOC LOG            50.80    20.79    10.87     4.61    29.07    11.56     7.22     0.77    40.90    11.09     9.16     2.43    45.11 [illegible] [illegible] [illegible]
TOC LOG RATE /HR   [illegible] [illegible] [illegible] [illegible] [illegible] 0.03 [illegible] 0.03 0.40 -0.02 0.07 [illegible] [illegible] [illegible] [illegible] [illegible]
COLOR REMOVAL %        46.67    12.50    44.19    12.97    55.56    42.50    13.04    65.00    49.33    42.11    11.21    25.60    50.00    35.62    17.24    32.35
TOTAL REMOVAL %        77.33      0.0      0.0      0.0    92.22      0.0      0.0      0.0    80.62      0.0      0.0      0.0    80.67      0.0      0.0      0.0
TOC REMOVAL %          37.88    21.14     3.09    17.02    46.35     7.20    29.31    12.20    55.17    -4.61    19.27    20.45    38.01    11.68    13.22    16.19
TOTAL REMOVAL %        60.61      0.0      0.0      0.0    69.10      0.0      0.0      0.0    69.83      0.0      0.0      0.0    60.18      0.0      0.0      0.0
BOD REMOV BASN %         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
BOD REMOV COLS %         0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
COLOR REM % SYST   [illegible] [illegible] [illegible] [illegible] 55.56 18.89 3.33 14.44 49.33    21.33 [illegible]   6.67    50.00    17.81 [illegible] [illegible]
TOC REM % SYS IN       37.88    13.13     1.52     8.08    46.35     3.86    14.59     4.29    55.17    -2.16     9.05     7.76    38.01     7.24     7.24     7.69
COLOR % OF FEED        53.33    46.67    26.04    22.67    44.44    25.56    22.22     7.78    50.67    29.33    26.04    19.38    50.00    32.19    28.57    19.33
TOC % OF FEED          62.12    48.99    47.47    39.39    53.65    49.79    35.19    30.90    44.83    46.98    37.93    30.17    61.99    54.75    47.51    39.82
OPERATING DAY #       141.00      0.0      0.0      0.0   142.00      0.0      0.0      0.0   143.00      0.0      0.0      0.0   144.00      0.0      0.0      0.0
COLOR RATE TOT%        65.23    65.23    65.23    65.23    99.44    99.44    99.44    99.44    87.23    87.23    87.23    87.23    66.18    66.18    66.18    66.18
TOC LOG RATE TOC        9.00     9.00     9.00     9.00    12.86    12.86    12.86    12.86    15.58    15.58    15.58    15.58     6.94     6.94     6.94     6.94

DISK FILE LOC#           401      402      403      404      405      406      407      408      409      410      411      412      413      414      415      416
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APPENDIX F

PRINTOUT OF DAILY SUMMARIES OF CONDITIONS AND RESULTS FOR LIME TREATMENT

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RR012C - WATER TREATMENT PILOT PLANT - LIME TREATMENT
                        BASIN    TRTOR    CARBR    PHA+F      BASIN    TRTOR    CARBR    PHA+F      BASIN    TRTOR    CARBR    PHA+F      BASIN    TRTOR    CARBR    PHA+F
DATE                     9.02      0.0      0.0      0.0       9.03      0.0      0.0      0.0       9.04      0.0      0.0      0.0       9.05      0.0      0.0      0.0
TIME OF DAY              7.30      0.0      0.0      0.0      12.30      0.0      0.0      0.0      12.30      0.0      0.0      0.0       7.30      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
WATER FLOW GPM            0.0    12.25      0.0      0.0        0.0    12.25      0.0      0.0        0.0    12.25      0.0      0.0        0.0    12.25      0.0      0.0
           HRS            0.0    24.25      0.0      0.0        0.0    29.00      0.0      0.0        0.0    23.50      0.0      0.0        0.0    19.50      0.0      0.0
TEMP WATER F            84.00    84.00      0.0      0.0      95.00    95.00      0.0      0.0      94.00    94.00      0.0      0.0      91.00    91.00      0.0      0.0
CA(OH)2 USED LB           0.0    60.00      0.0      0.0        0.0   100.00      0.0      0.0        0.0    70.00      0.0      0.0        0.0    56.00      0.0      0.0
        FED LB/HR         0.0     2.48      0.0      0.0        0.0     3.45      0.0      0.0        0.0     2.98      0.0      0.0        0.0     2.87      0.0      0.0
        DOSE MG/L         0.0   405.00      0.0      0.0        0.0   563.00      0.0      0.0        0.0   486.00      0.0      0.0        0.0   469.00      0.0      0.0
SLUDGE REMOV GAL          0.0     2.00      0.0      0.0        0.0   140.00      0.0      0.0        0.0      0.0      0.0      0.0        0.0    10.00      0.0      0.0
   DENSITY G/ML           0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
   % DRY SOLIDS           0.0    13.20      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0    15.60      0.0      0.0
   % CA IN SOLID          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
CO2 USED LB               0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
LIME MIX WAT GPM          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
FIL SOLIDS  MG/L          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
    IN TRTR MG/L          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
COLOR FPC AT PH       1050.00   900.00      0.0      0.0     750.00   690.00      0.0      0.0    1125.00   600.00      0.0      0.0     1050.001275.00      0.0      0.0
      MPC AT PH        750.00   480.00      0.0      0.0     608.00   396.00      0.0      0.0     743.00   410.00      0.0      0.0     713.00   428.00      0.0      0.0
      MPC PH 7.6       615.00   289.00      0.0      0.0     585.00   210.00      0.0      0.0     537.00      0.0      0.0      0.0     590.00   244.00      0.0      0.0
TOC FP MG/L            173.00   130.00      0.0      0.0     145.00   106.00      0.0      0.0     169.00   117.00      0.0      0.0     154.00   127.00      0.0      0.0
TIC FP MG/L             57.00    10.00      0.0      0.0      53.00    10.00      0.0      0.0      57.00     9.00      0.0      0.0      56.00     9.00      0.0      0.0
CA  MP MG/L              8.12    41.50      0.0      0.0      10.14    44.80      0.0      0.0       7.04    66.00      0.0      0.0       5.12    44.40      0.0      0.0
PH                       9.30    11.60      0.0      0.0       9.30    11.60      0.0      0.0       9.40    11.75      0.0      0.0       9.50    11.60      0.0      0.0
BOD     MG/L              0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
COND MICROMHOS        1030.001890.00      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
TURBIDITY JTU           25.00    90.00      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
VOLATILES MEOH            0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
          FORMALD         0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
          ACETIC          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
CUM HR OPERATED           0.0   1121.001121.00      0.0        0.0   1150.001150.00      0.0        0.0   1173.501173.50      0.0        0.0   1193.001193.00      0.0
CUM FLOW KGAL             0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
CUM LIME USED LB          0.0  7632.00      0.0      0.0        0.0  7732.00      0.0      0.0        0.0  7802.00      0.0      0.0        0.0  7858.00      0.0      0.0
CU7.6 REMOVD %BA          0.0    53.01      0.0      0.0        0.0    64.10      0.0      0.0        0.0      0.0      0.0      0.0        0.0    58.64      0.0      0.0
TOC REMOVED %BA           0.0    24.86      0.0      0.0        0.0    26.90      0.0      0.0        0.0    30.77      0.0      0.0        0.0    17.53      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
CAO DOSE MG/L             0.0   307.80      0.0      0.0        0.0   427.88      0.0      0.0        0.0   369.36      0.0      0.0        0.0   356.44      0.0      0.0
SLUDGE REMOVD LB          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
   SOLIDS REM LB          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
CA BASN WAT MG/L          0.0     8.12      0.0      0.0        0.0    10.14      0.0      0.0        0.0     7.04      0.0      0.0        0.0     5.12      0.0      0.0
   IN LIME  MG/L          0.0   218.70      0.0      0.0        0.0   304.02      0.0      0.0        0.0   262.44      0.0      0.0        0.0   253.26      0.0      0.0
   PROD WAT MG/L          0.0    41.50      0.0      0.0        0.0    44.80      0.0      0.0        0.0    66.00      0.0      0.0        0.0    44.40      0.0      0.0
   SLUDGE   MG/L          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
% FEED CA TO WAT          0.0    18.98      0.0      0.0        0.0    14.74      0.0      0.0        0.0    25.15      0.0      0.0        0.0    17.53      0.0      0.0
          TO SLDG         0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
TOC SLDG SOLDS %          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
                          0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0        0.0      0.0      0.0      0.0
JULIAN                 245.00      0.0      0.0      0.0     246.00      0.0      0.0      0.0     247.00      0.0      0.0      0.0     248.00      0.0      0.0      0.0
DISC FILE LOCN          50.00      0.0      0.0      0.0      51.00      0.0      0.0      0.0      52.00      0.0      0.0      0.0      53.00      0.0      0.0      0.0
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APPENDIX G
PRINTOUT OF DAILY SUMMARIES OF CONDITIONS AND RESULTS FOR LIME-CARBON SEQUENCE

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RR0128 - WATER TREATMENT PILOT PLANT - LIME CARBON SEQUENCE
DATE                 |   8.23     0.0  |   8.24     0.0  |   8.25     0.0  |   8.26     0.0  |   8.27     0.0  |   8.28     0.0  |   8.29     0.0
TIME OF DAY          |   8.00     0.0  |   8.00     0.0  |   8.00     0.0  |   8.00     0.0  |  16.30     0.0  |   8.00     0.0  |   8.00     0.0
COLUMN NAME   A=1    |   4.00    3.00  |   4.00    3.00  |   4.00    3.00  |   4.00    3.00  |   4.00    3.00  |   4.00    3.00  |   4.00    3.00
HRS OPERATED         |  24.00   24.00  |  22.50   22.50  |  24.00   24.00  |  23.00   23.00  |  33.50   33.50  |  14.50   14.50  |  22.50   22.50
FLOW RATE GPM        |  10.00     0.0  |  10.00     0.0  |  10.00     0.0  |  10.00     0.0  |  10.00     0.0  |  10.00     0.0  |  10.00     0.0
TEMP COLUMN F        |  90.00     0.0  |  90.00     0.0  |  91.00     0.0  |  87.00     0.0  |  98.00     0.0  |  92.00     0.0  |  90.00     0.0
CU FM BASIN FPC      |1125.00     0.0  | 943.50     0.0  |1275.00     0.0  |1350.00     0.0  |1125.00     0.0  |1050.00     0.0  |1125.00     0.0
                MPC  | 900.00     0.0  | 720.00     0.0  | 713.00     0.0  | 975.00     0.0  | 638.00     0.0  | 720.00     0.0  | 900.00     0.0
CU TO COL  FPC       | 525.00  188.00  | 900.00  600.00  | 720.00  341.00  | 630.001350.00  | 630.00  327.00  | 900.00  443.00  |1050.00  645.00
           MPC       | 248.00  154.00  | 293.00  210.00  | 259.00  210.00  | 270.00  180.00  | 263.00  203.00  | 252.00  203.00  | 252.00  233.00
CU FM COL  FPC       | 188.00   87.00  | 600.00  240.00  | 341.00  165.00  |1350.00  203.00  | 327.00  188.00  | 443.00  278.00  | 645.00  428.00
           MPC       | 154.00   64.00  | 210.00  143.00  | 210.00  102.00  | 180.00  117.00  | 203.00   98.00  | 203.00  135.00  | 233.00  180.00
TOC  FM BASIN        | 165.00     0.0  | 151.00     0.0  | 145.00     0.0  | 147.00     0.0  | 156.00     0.0  | 164.00     0.0  | 167.00     0.0
     TO COL          | 105.00   96.00  | 108.00  100.00  | 100.00   85.00  | 111.00  107.00  | 112.00  103.00  | 119.00  108.00  | 126.00  110.00
     FM COL          |  96.00   68.00  | 100.00   67.00  |  85.00   64.00  | 107.00   73.00  | 103.00   68.00  | 108.00   83.00  | 110.00   85.00
CA  FM BASIN         |  10.00     0.0  |  12.70     0.0  |  11.60     0.0  |  13.50     0.0  |   7.10     0.0  |   7.30     0.0  |   9.40     0.0
    TO/FROM COLS     | 117.00     0.0  |  68.00     0.0  |  76.60     0.0  |  65.40     0.0  |  62.60     0.0  |  15.20     0.0  |  18.40     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
TIC  FM BASIN        |  57.00     0.0  |  55.00     0.0  |  57.00     0.0  |  59.00     0.0  |  58.00     0.0  |  58.00     0.0  |  59.00     0.0
     TO/FM COLS      |  15.00   12.00  |  16.00   11.00  |  16.00   16.00  |  13.00   14.00  |  16.00   12.00  |  13.00    8.00  |  10.00    9.00
BOD  TO/FM COLS      |    0.0     0.0  |    0.0  125.00  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
PH  FM BASIN         |   9.80     0.0  |   9.50     0.0  |   9.60     0.0  |   8.70     0.0  |   9.40     0.0  |   9.40     0.0  |   9.60     0.0
    TO/FM COLS       |  12.30   12.30  |  11.70   11.70  |  12.10   12.10  |  11.30   11.30  |  11.00   11.40  |  11.20   11.30  |  11.30   11.30
COND TO/FM MMHOS     |3000.00     0.0  |2108.00     0.0  |2220.00     0.0  |1520.00     0.0  |1190.00     0.0  |1790.00     0.0  |1820.00     0.0
TURB TO/FM JTU       |  22.00     0.0  |  34.00     0.0  |  28.00    7.00  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
PRESS DROP COLS      |   3.02    1.01  |   2.00    1.00  |   4.02    1.01  |   2.00    1.00  |   2.00    1.00  |   3.01    1.01  |   2.00    1.00
                F1   |   8.03     0.0  |   2.00     0.0  |   4.02     0.0  |   3.00     0.0  |   4.00     0.0  |   5.01     0.0  |   3.00     0.0
CAOH2 DOSE MG/L      | 619.00     0.0  | 454.00     0.0  | 477.00     0.0  | 477.00     0.0  | 514.00     0.0  | 514.00     0.0  | 516.00     0.0
VOLATILES MEOH       |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
          ACETALD    |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
          ACETIC     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
CUM HRS OPTD         |1176.50  646.50  |1199.00  669.00  |1223.00  693.00  |1246.00  716.00  |1279.50  749.50  |1294.00  764.00  |1316.50  786.50
CUM FLOW MGAL        | 748.80  403.20  | 763.20  417.60  | 777.60  432.00  | 792.00  446.40  | 806.40  460.80  | 820.80  475.20  | 835.20  489.60
MPC LOADED  CU/G     |   7.06    6.76  |   5.85    4.72  |   3.68    8.11  |   6.48    4.54  |   6.29   11.01  |   2.22    3.09  |   1.34    3.79
    CUM LDG          | 516.18  248.48  | 522.02  253.20  | 525.70  261.31  | 532.18  265.85  | 538.47  276.86  | 540.70  279.94  | 542.03  283.67
    LDG RATE /HR     |   0.29    0.28  |   0.26    0.21  |   0.15    0.34  |   0.28    0.20  |   0.19    0.33  |   0.15    0.21  |   0.06    0.17
    RATE TOT *C      |  57.59     0.0  |  46.95     0.0  |  49.14     0.0  |  47.89     0.0  |  51.64     0.0  |  36.62     0.0  |  22.54     0.0
   -REM % SYS IN     |  37.90   36.29  |  28.33   22.87  |  18.92   41.70  |  33.33   23.33  |  22.91   39.92  |  19.44   26.98  |   7.54   21.03
    TOT REM % IN     |  74.19     0.0  |  51.19     0.0  |  60.62     0.0  |  56.67     0.0  |  62.74     0.0  |  46.43     0.0  |  28.57     0.0
    REM % TO COL     |  37.90   58.44  |  28.33   31.90  |  18.92   51.43  |  33.33   35.00  |  22.91   51.72  |  19.44   33.50  |   7.54   22.75
TOC LOADED MG/G      |   0.68    2.10  |   0.56    2.32  |   1.13    1.58  |   0.29    2.45  |   0.94    3.67  |   0.50    1.13  |   1.13    1.76
    CUM LDG          | 144.11   59.00  | 144.67   61.33  | 145.80   62.91  | 146.08   65.35  | 147.03   69.02  | 147.53   70.16  | 148.65   71.92
    LDG RATE /HR     |   0.03    0.09  |   0.03    0.10  |   0.05    0.07  |   0.31    0.11  |   0.03    0.11  |   0.03    0.08  |   0.05    0.08
    RATE TOT *C      |  11.58     0.0  |  12.83     0.0  |  11.27     0.0  |  11.89     0.0  |  13.77     0.0  |  11.27     0.0  |  12.83     0.0
   -REM % SYS IN     |   8.57   26.67  |   7.41   30.56  |  15.00   21.00  |   3.60   30.63  |   8.04   31.25  |   9.24   21.01  |  12.70   19.84
    TOT REM % IN     |  35.24     0.0  |  37.96     0.0  |  36.00     0.0  |  34.23     0.0  |  39.29     0.0  |  30.25     0.0  |  32.54     0.0
    REM % TO COL     |   8.57   29.17  |   7.41   33.00  |  15.00   24.71  |   3.60   31.78  |   8.04   33.98  |   9.25   23.15  |  12.70   22.73
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
                     |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0  |    0.0     0.0
JULIAN DAY           | 235.00     0.0  | 236.00     0.0  | 239.00     0.0  | 238.00     0.0  | 239.00     0.0  | 240.00     0.0  | 241.00     0.0
DISK FILE LOC        |  59.00     0.0  |  60.00     0.0  |  61.00     0.0  |  62.00     0.0  |  63.00     0.0  |  64.00     0.0  |  65.00     0.0
```

APPENDIX H

GENERALIZED PROCEDURE FOR DESIGNING PLANT FOR TREATING KRAFT PULP MILL EFFLUENT BY ADSORPTION IN GRANULAR ACTIVATED CARBON COLUMNS

1. Determine the flow and quality of the water to be treated.

Normally, the plant is designed to treat the average of the daily maximum flow rates and to treat water with the average maximum color and TOC concentrations. Other properties of the effluent should also be determined: BOD, conductivity, settleable solids, suspended solids, pH, temperature, etc.

Determine what concentrations of color and TOC are to be tolerated in the treated water. The design of the carbon adsorption plant for a given flow rate is greatly affected by the prior treatment of the effluent water (clarification alone, lime treatment, or bio-oxidation) and by the permissible concentrations of color and TOC in the product water from the carbon treatment.

2. Select type of carbon.

The type of carbon is determined from extensive laboratory isotherm tests and preferably from bench-scale column adsorption tests after a preliminary selection based on previous experience, price, service provided by manufacturer, resistance to abrasion, and other factors. The mesh size should probably be about 20 x 40 mesh, since this size minimizes the retention time required and yet does not cause appreciable pressure loss at flow velocities of 1 - 4 gpm/ft^2.

2. Contact time and flow velocity.

Determine from pilot-plant or bench-scale column adsorption tests the contact time that is required at flow velocities of 1 - 4 gpm/ft^2 of column area to meet the desired properties of the treated water. The value of retention time dictates the volume of the carbon needed for the plant and is the major determinant of capital costs of the plant.

4. Dosage of carbon per unit of water treated.

The dosage is the pounds of regenerated carbon that must be added to the adsorbers (and loaded carbon that is removed) per 1000 gal of water treated to maintain the desired quality of product water. The dosage rate is a major determinant of operating costs since losses (make-up) of carbon and regeneration costs are directly related to the dosage. The dosage is best determined from bench-scale or pilot plant adsorption tests with at least three columns in series operated at the expected flow-rate (gpm/ft^2) until it has been necessary to add 5 fresh columns while maintaining the desired product water concentration, or more generally 2 more columns than the number of columns in the adsorption train.

$$\text{dosage rate in lb/kgal} = \frac{\text{(lb carbon per column) x (total fresh columns added)}}{\text{total kgal of water treated}}$$

The rate can also be determined (with less reliability) from lab isotherms with at least 5 representative samples of the water to be treated. From the isotherms, determine average loading for the average feed concentration.

$$\text{dosage rate} = \frac{\text{(feed concentration - product concentration)}}{\text{0.65 (loading at feed concentration)}}$$

where: dosage is g carbon per 1 water
concentrations are in mg/1
loading is in mg/g carbon.

5. Volumetric flow rate and volume of carbon needed.

$$\text{Volumetric flow rate, } \frac{\text{vol. water}}{\text{hr x vol. carbon}} = \frac{1}{\text{C.T.}}$$

where C.T. = contact time, hr

$$\text{volume of carbon needed, ft}^3 = \text{(ft}^3\text{ water/hr) x C.T.}$$

$$= \text{0.125 gpm x C.T.}$$

$$\text{weight of carbon, lb} = \text{25 lb/ft}^3\text{ x vol. of carbon}$$

6. Design of carbon columns.

(See also EPA "Process Design Manual for Carbon Adsorption" October 1973(19))

Total cross sectional area of the columns, ft^2 = (water flow in gpm)/(velocity in gpm/ft^2).

$$\text{Diameter of columns } \sqrt{\frac{\text{4 (area of columns)}}{3.14}}$$

Use multiple trains of columns in parallel flow to give height/diameter ratio between 1 and 3.

Total length of carbon bed, ft = 8(gpm/ft^2) x C.T.
or length = (vol. carbon)/(total area)

Length of bed in each column = total length/number of columns --(minimum of three columns) in series to provide adequate counter-current contacting.

Freeboard in columns for backwash bed expansion = 50% of carbon bed.

Extra columns for regeneration -
a minimum of 2 columns is required to function as feed and receiving column for the regeneration furnace. Two columns can serve several trains if provided with proper piping arrangements.

Extra columns for peak load -
provide 10 to 30% extra columns, depending on anticipated variability of flow and concentration. Consider separate system for pre-dampening fluctions by storage and/or spill control.

Down-flow or up-flow of water in columns. With proper backwashing, down-flow appears preferable.

Backwash - use velocity that expands the carbon bed 20 to 50%. This value is about 10 gpm/ft^2 for 20 x 40 mesh Darco carbon. For backwash inlet distributor, graded gravel and sand is recommended, but other types of carbon support are available and probably satisfactory. The period of backwashing for each column should be about 20 minutes every 48 hours. Provide air at start of backwash to break up any clumps that might have formed.

Weight of carbon per column, lb = (area, ft^2) x (bed height, ft) x (density, lb/ft^3)

Frequency of column change per train, days =

$$\frac{\text{(wt. of carbon per column, lb)}}{\text{(dosage, lb/kgal) (flow per train, kgal/day)}}$$

Retention time of carbon in train, days =

$$\frac{\text{(wt. of carbon per train, lb)}}{\text{(dosage, lb/kgal)(flow per train, kgal/day)}}$$

7. Total inventory of carbon.

Total carbon = (no. of columns) x (volume of each) x (density of carbon)= weight of carbon needed. Warehousing will require additonal carbon; the amount being dependent on the purchase requirements.

8. Make-up carbon.

The make-up carbon is equal to the loss of carbon during removal from columns and in regeneration. This loss runs 5 - 10% of the carbon dosage or weight of carbon that is regenerated. It is expected that the loss will probably be near 5% for large plants treating pulp mill effluents.

9. Carbon regeneration plant.

a. Capacity, lb/day = (carbon dosage, lb/kgal) x (water flow, kgal/day)

b. Type of furnace - a multiple-hearth furnace is generally used. There are three major manufacturers.

c. Operating conditions - selected by consultants or through trials by furnace manufacturer.

APPENDIX I

RELATIONSHIPS USEFUL IN DESIGN OF DOWNFLOW CARBON ADSORPTION COLUMNS

Superficial (empty column) velocity, ft/hr = $8(\text{gpm/ft}^2)$

Total cross-sectional area of columns = $\text{gpm}/(\text{gpm/ft}^2)$

Bed Height, ft

= (lineal velocity, ft/hr) (contact time, hr)

= $8(\text{gpm/ft}^2)$ (contact time, hr)

Volumetric flow rate,by/hr = (vol water/hr)/(vol carbon) = $\dfrac{1}{\text{contact time,hr}}$

= $8(\text{gpm/ft}^2)/(\text{bed height})$

Bed height or length = $\dfrac{0.02 \times \text{flow} \times \Delta C}{\text{rate}}$

Where: Flow = water flow rate, gpm/ft^2

ΔC = inlet - outlet concentrations in mg/l

rate = rate of adsorption in $\dfrac{\text{mg}}{\text{g} \times \text{hr}}$

This relationship is generally applicable, but the rate must apply at the flow rate used and over the concentration range used.

APPENDIX J

ESTIMATE NO. 1. - MICROLIME-CARBON TREATMENT OF 9.6 MGD OF EFFLUENT FROM A NEW 800 TON/DAY UNBLEACHED KRAFT PULP AND PAPER MILL

MAJOR CONDITIONS AND ASSUMPTIONS

Flow Sheet - See Figure 30

Lime Treatment

Microlime treatment is used
Dosage = 520 mg/l CaO (approximate)
Rise rate = 700 gpd/ft^2
Water quality:

	Feed	Product	% Reduction
Color, CU	1000	300	70
TOC, mg/l	250	150	40
BOD, mg/l	250	225	10
pH	10.5	11.5	
Conductivity, micromhos	1200	3600	
Susp. solids, mg/l	200	250	
Temperature, ^{o}F	100	100	

Lime sludge dewatered to 70% solids and returned to lime kiln. Includes capital cost of new lime kiln for the proportion of load added by effluent treatment sludge.
Desgin basis for lime treatment includes data from Interstate Paper Company (5,18) and Continental Can Company (14) on lime treatment of kraft mill effluents. Capital costs for lime treatment are derived from costs of the Continental Can Company lime treatment plant at Hodge, La.

Carbon Adsorption

Water quality, average composition:

	Feed	Product	% Reduction by carbon	% Reduction overall
Color, CU	300	100	67	90
TOC, mg/l	150	100	33	60
BOD, mg/l	225	150	33	40
pH	11.5	8.0*		
Temperature, ^{o}F	100	100		
Susp. solids, mg/l	250	15		

*Product water is carbonated to pH 8

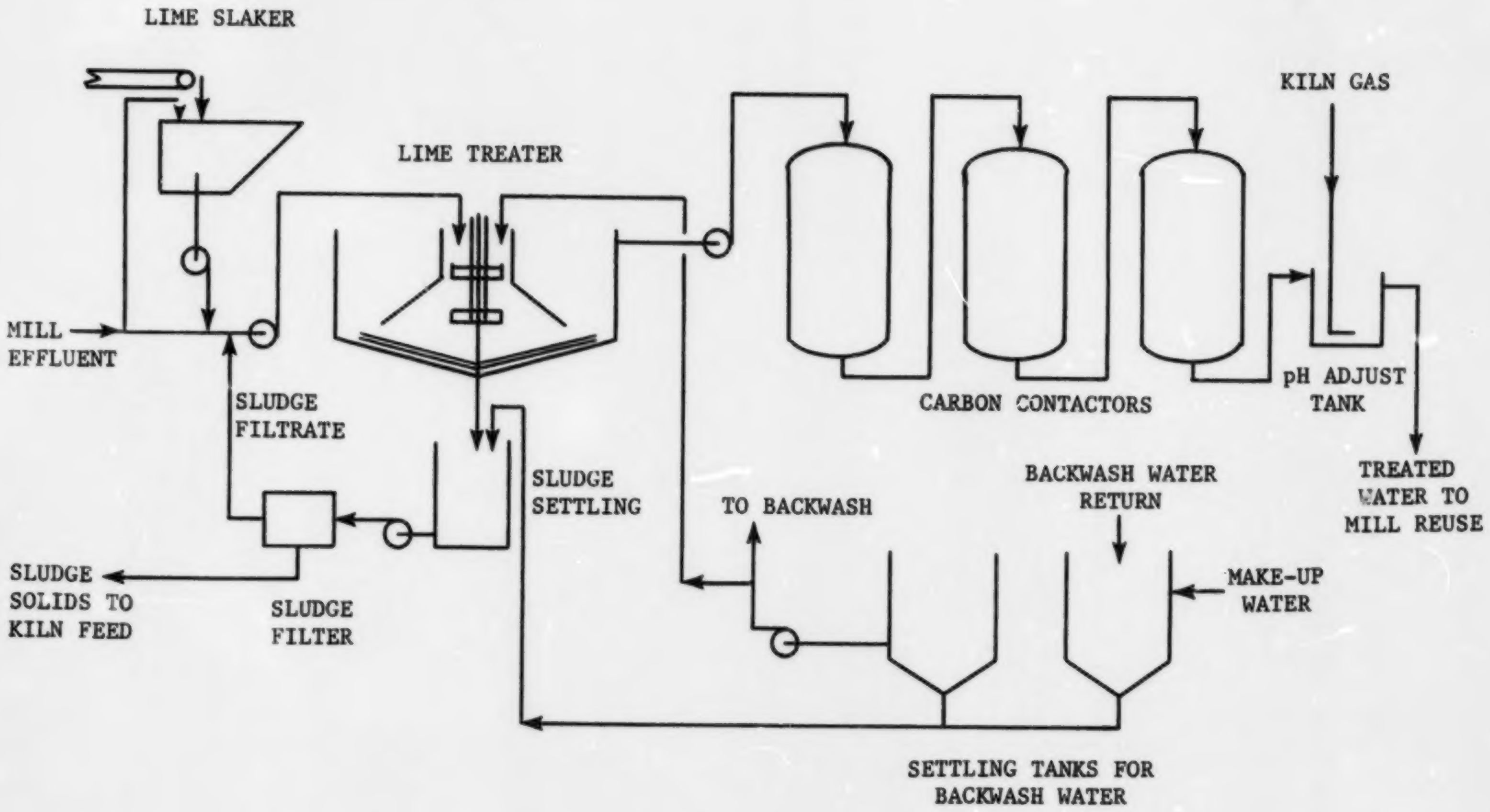

LIME SLAKER
LIME TREATER
KILN GAS
MILL EFFLUENT
SLUDGE FILTRATE
CARBON CONTACTORS
pH ADJUST TANK
SLUDGE SETTLING
TO BACKWASH
BACKWASH WATER RETURN
TREATED WATER TO MILL REUSE
MAKE-UP WATER
SLUDGE SOLIDS TO KILN FEED
SLUDGE FILTER
SETTLING TANKS FOR BACKWASH WATER

Figure 30. Flow diagram for microlime-carbon treatment of unbleached kraft effluent for reuse

Designed for average flow of 9.6 mgd and maximum flow of 30% greater, or 12.5 mgd.
Designed for average concentrations above, but with excess capacity for greater concentration of color and TOC.
Down-flow, fixed-bed, pressure carbon contactors (columns).
Air and water backwashing of columns.
Feedwater to columns is not filtered.
Product water is adjusted to pH 8 by addition of kiln gas.
Carbon used: 20 x 40 mesh, equivalent to that used in pilot plant.
Make-up (loss) of carbon per regeneration = 5%.
Contact time, volume of carbon needed, and dosage rate are based on pilot plant results.
Capital costs for carbon adsorption plant are based on cost data given in FWPCA Report TWRC-11 (17) prepared by M. W. Kellogg Company and in EPA Process Design Manual for Carbon Adsorption, October, 1973 (19).
Cost of make-up carbon = \$0.27/lb and \$0.10/lb.

Costs for Complete Plant

Capital costs include equipment, installation, instrumentation, buildings, engineering, contractor overhead and profit.
Time basis for cost = January, 1973 adjusted by Engineering News Record Construction Cost Index.
Amortization = 16 years, straight line = 6.25% of total capital investment per year.
Repairs and maintenance = 3% of total capital investment per year.
Taxes and Insurance = 2% of total capital investment per year.
Plant overhead = 75% of direct labor cost.
Steam = \$0.80/1000 lb, electricity = \$0.01/kwh, gas = \$0.60/10^6 Btu.

DESIGN OF LIME TREATMENT UNIT

Lime Dosage - to maintain 80 mg/l dissolved Ca in water leaving lime treater. On basis of pilot plant treatment of unbleached kraft total mill effluent, average dosage is 520 mg/l CaO, or 0.52 x 8.34 = 4.33 lb/1000 gal, or 4.33 x 9,600/2000 = 20.8 tons CaO.

Lime Slaker and Feeder

Mill lime is fed to a lime slaking tank to maintain a constant 10% solids slurry which is then fed through a controlled slurry feeder to the effluent line going to the lime treater. The soluble calcium concentration in the lime treated water is controlled by a sensor in the lime treater which sends a signal to the slurry which is then fed through a controlled slurry feeder to the effluent line going to the lime treater. The soluble calcium concentration in the lime treated water is controlled by a sensor in the lime treater which sends a signal to the slurry feeder to maintain the calcium concentration at 80 ± 10 mg/l Ca.

Lime Treater

A conventional reactor-clarifier is used that has an enlarged center-well for the reaction of lime with the organic compounds of the effluent and for reaction and growth of $CaCO_3$ crystals.

Volume of reaction zone to give 30 min. retention =

$$30 \times \frac{9,600,000}{1440} = 200,000 \text{ gal.}$$

Top area of reaction zone that has enlarged top section is estimated to be 670 ft^2, or 29 ft in diameter.

Area of clarifier section at rise rate of 700 gpd/ft^2 =

$$\frac{9,600,000}{700} = 13,700 \text{ ft}^2$$

Total area of lime treater = 14,370 x 4/3.14 = 135 ft.

Lime Balance for Lime-Carbon Treatment

	Conc'n. in water	
	Ca, mg/l	CaO, mg/l
In feed water	12	17
Lime added to lime treater	372	520
Soluble in product water	80	112
In suspended solids from lime treater[a]	50	70
Loss in sludge handling[b]	19	26
Net recovered in sludge to kiln[c]	286	400

Overall recovery of CaO = 100 x 400/520 = 77%

[a] At 20% Ca in suspended solids, or 0.20 x 250 = 50 mg/l Ca. This calcium is recovered as sludge from backwashing of carbon column which is added to the lime-treater sludge.

[b] Estimated loss = 5% of added lime, or 0.05 x 520 = 26 mg/l CaO

[c] 520 + 17- 112 -25 = 400 mg/l CaO

Sludge Composition

On the basis of pilot-plant results, the sludge will consist of these materials:

	Conc'n in water	
	mg/l	lb/kgal
$CaCO_3$ from $CO_3^=$ in feed water	343	2.85
Ca-organics	278	2.32
Susp. solids in feed water[a]	200	1.67
Total sludge solids produced	821	6.84

[a] Mainly inorganic solids

CaO in lime sludge solids to kiln = 400 mg/l of water treated (see above) or 100 x 400/821 = 49% CaO

Total sludge solids produced = 6.84 x 9600/2000 = 32.8 tons/day

CaO in sludge = 32.8 x 0.49 = 16.1 tons/day

Volume of sludge produced at 15% solids from lime treater

$$6.84 \times 9600 \times \frac{1}{0.15} \times \frac{1}{8.34} \times \frac{1}{1.09 \text{ sp. gr.}} = 48{,}200 \text{ gal/day} = 33.5 \text{ gpm}$$

Sludge Tank for Settling - at 12-hour retention and 30% solids =

$$\frac{48{,}200}{2} \times \frac{15}{30} = 12{,}000 \text{ gal.}$$

Sludge Filters - on the basis of pilot plant experience, the sludge filters readily, presumably because microlime gives a high percentage of $CaCO_3$ in the sludge, as compared to minilime treatment.

On the basis of the pilot-plant results, assume sludge from sludge tank will contain 25% solids and will filter at a rate of 100 lb/hr ft^2 on wire-drum filter.

$$\text{Area of filter} = \frac{6.84 \text{ lb/kgal} \times 9{,}600 \text{ kgal/day}}{24 \text{ hr/day} \times 100 \text{ lb/hr ft}^2} = 27.4 \text{ ft}^2$$

(Possibly, the settled sludge could be added to the mill's lime mud filter).

DESIGN OF CARBON ADSORPTION UNITS

Contact Time Required

Average pilot-plant results show that when removing color from 300 to 100 CU when the calcium content of the water was about 80 mg/l Ca, the length of adsorption bed at a superficial flow rate of 1.4 gpm/ft^2 was 19 ft and the contact time was 1.7 hr. The data showed that a slightly shorter length of bed was required to reduce the TOC from 150 to 100 mg/l. Therefore, use a contact time of 1.7 hr plus 7% excess or 1.8 hr. (An additional 20% excess capacity is allowed later as spare columns.)

Selections of Velocity, Pressure Drop, and Length of Carbon Bed.

Pilot plant data showed that it is desirable to use a superficial velocity greater than 2 gpm/ft^2 to provide increased turbulence and adsorption rates. However, as velocity is increased, the length required increased in direct relation to velocity (to maintain constant contact time) and the pressure drop is increased by both the increased length and greater velocity. The following tabulation shows the effect of flow rate on pressure drop, as determined from Fig. 3-4 of the EPA Design Manual for Carbon Adsorption (18) for the desired contact time of 1.8 hr (0.56 V/V hr) when using 20 x 40 mesh carbon.

Flow rate, gpm/ft^2	Length of bed required, ft	Pressure drop, psi
1.4	20	1.1
2.8	40	4.2
4.2	60	9.7
5.6	80	18.1

To provide a fairly low pressure drop of 9.7 psi, a flow rate of 4.2 gpm/ft^2 is selected, which requires a total length of bed of carbon of 60 ft.

The effect of velocity on adsorption rates was not studied in the pilot plant for the microlime-carbon sequence, while operations were carried out at 1.4 gpm/ft^2. Based on increased adsorption rates, or decreased retention times, observed for increased flow rate in the primary-carbon pilot plant work, it is possible that the design flow rate of 4.2 gpm/ft^2 chosen above in conjunction with contact time requirements based on 1.4 gpm/ft^2 in the pilot plant, could represent a sizeable effective excess contact time.

Dimensions of Adsorption Columns

Area = 6670 gpm/4.2 gpm/ft^2 = 1590 ft^2 total.

No. of parallel trains - use 3 to keep diameter of columns at reasonable size.

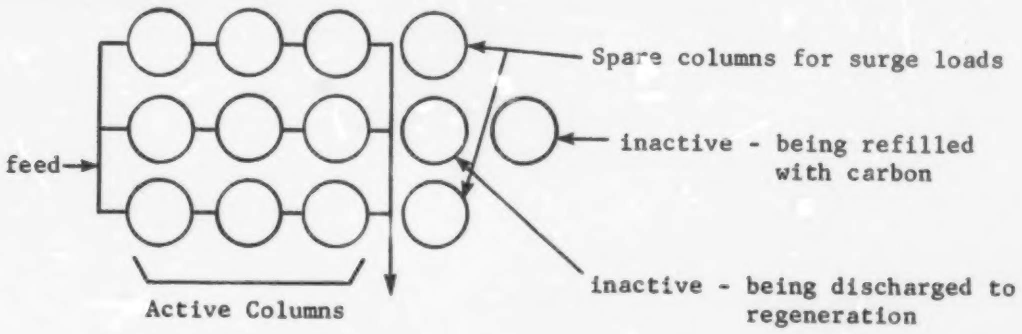
Diameter of each column = $\frac{1590 \times 4}{3 \times 3.14}$ = 26 ft.

No. of columns in series per train - use 3 to provide adequate countercurrent contacting and to keep the ratio of height to diameter about 1.

Height of bed in each adsorber = $\frac{60}{3}$ = 20 ft.

Total height of each column, allowing 50% free board for bed expansion during backwashing = 20 x 1.5 = 30 ft.

Arrangement of Columns


Spare columns for surge loads
inactive - being refilled with carbon
feed
inactive - being discharged to regeneration
Active Columns

Total columns = 13
Active columns = 9
Spare columns = 2
Ready to have carbon discharged = 1
Ready to receive regenerated carbon = 1
Total columns with carbon = 12

Volume of carbon per column = $\frac{3.14 \times 26^2 \times 20}{4}$ = 10,600 ft^3.

Weight of carbon per column = 10,600 x 25 lb/ft^3 = 265,000 lb.

Total weight of carbon in system = 12 x 265,000 = 3,180,000 lb.

Excess capacity available for surge loads
= 2 columns out of 9 active columns = 22% excess.

Total excess capacity for surge loads
22% excess columns
7% extra contact time (above)
- 4% lost capacity during backwash (below)
25% net excess capacity.

Column Features

Columns are field erected steel columns, tested to hold 70 psi, dished heads, with 8-mil interior coating of epoxy-tar, or equivalent, with gravel support for carbon, and with piping connections for backwashing for changing the flow sequence through the columns, and for movement of carbon as slurry to and from regeneration.

Backwashing of Columns

On the basis of pilot plant experience and results from commercial carbon adsorption for treating municipal effluents, the 3 lead columns are backwashed once each day and the remaining 6 columns are backwashed every two days. Total number of columns backwashed per day = 6. During each backwash, each column is agitated with a short backwash of compressed air and then with a flow of water at 10 gpm/ft^2 (5300 gpm) for 15 minutes.

Volume of water used per backwashing = 15 x 5300 = 80,000 gal.
Void volume of each column at 50% voids in carbon
= 10,600 ft^3 carbon x 0.5 + 5300 ft^3 freeboard = 10,600 ft^3
= 10,600 x 7.5 gal/ft^3 = 80,000 gal.
So backwashing displaces an equal volume of water from the column.

Backwash Schedule

A schedule is arranged to meet above backwashing requirements by backwashing the No. 3 and No. 1 columns on one day and No. 2 and No. 1 columns on alternate days. One quantity of 80,000 gal of carbon-treated water is used each day; first for backwashing the No. 3 columns or No. 2 columns, then for No. 1 columns, and then pumped to the lime treater. The water from backwashing each column is discharged to a second 80,000-gal tank where a coagulant is added and the suspended solids removed by settling and the sludge is pumped to the lime sludge tank. The clarified water is used for backwashing the next column and is then discharged to the other settling tank. Thus two settling tanks are needed to permit partial reuse of the backwash water.

Columns backwashed per day = 6, or 2 each shift.
Product water used = 80,000 gal/day = $\frac{100 \times 80{,}000}{9{,}600{,}000}$ = 0.8% of daily production.

Total off-time of columns for backwashing at 20 minutes per set of columns x 2 = 40 minutes/day = 3% of time.
Total loss of production for backwashing = 3.0 + 0.8 = 3.8%.

Carbon Dosage Rate

The pilot plant runs for microlime-carbon required 2.5 lb/kgal to reduce color 230 to 70 CU and TOC 170 to 110 mg/l.
Since this design calls for about the same removals, use a dosage of 2.5 lb/kgal.
Carbon added = 2.5 x 9,600 kgal/day = 24,000 lb/day = 1000 lb/hr.

Carbon Make-Up Rate

Most commercial carbon adsorption units experience a loss of about 5% per generation, so use this.

$$0.05 \times 24{,}000 = 1200 \text{ lb/day}$$

Regeneration of Carbon

Average rate = 24,000 lb/day = 1000 lb/hr.
Hours of operation per day = 24
Furnace - use multiple-hearth regeneration furnace with capacity of 100 lb/day/ft^2, which is based on full-scale plants for treating municipal wastewater.

Total hearth area with allowance for 20% down time (including 5% make up) $= \frac{24{,}000}{100} \times 1.2 = 290$ ft^2
No. of hearths - use 6
Area per hearth = 290 ft^2/6 = 48.3 ft^2

Diam. of furnace = $\sqrt{48.3 \times 4/3.14} = 8$ ft.

CAPITAL COST OF LIME TREATMENT UNIT

The most reliable cost data on lime treatment is that for the Continental Can Company plant (35) which uses minilime treatment (1000 mg/l CaO) for 9 mgd of total mill effluent from a pulp and paper mill producing 750 tons/day. Their cost include all associated costs including capital cost for additional lime kiln capacity, engineering, contractor's overhead and profit, lime feeder and slaker, sludge dewatering, carbonation, and instrumentation.

Total cost of Continental Can lime treatment plant	$1,762,000
Adjusted to microlime system (lower lime rate, no carbonation, etc.)	1,182,000

Adjusted for lower rise rate in lime clarifier (use 700 rather than 980 gpd/ft^2)	$1,261,000
Adjusted from 9.0 to 9.6 mgd	1,328,000
Adjusted from 1972 to Jan. 1973 costs by ENR Construction Index, multiply by 1.09	1,448,000
Add 8% of cost of lime kiln for sludge lime added to mill lime kiln, adjusted to Jan. 1973 costs	232,000
Total cost for microlime treatment system	1,680,000

CAPITAL COSTS FOR CARBON ADSORPTION UNIT

The cost for the carbon adsorption unit is based on the study by M. W. Kellogg Co. for FWPCA in 1969 (17). In the Kellogg-FWPCA report the total installed plant cost was broken down into categories. In preparing this cost estimate, each of Kellogg costs were adjusted for the conditions used in this estimate. For example, the cost of carbon adsorbers (44% of the total Kellogg cost) was multiplied by 2.2, which is the ratio of volume of carbon in this estimate to that in the Kellogg estimate. The table below lists the categories of costs for both estimates and the multiplying factor used in adjusting the Kellogg costs to this estimate. The multiplying factors include, where applicable, a ratio of sizes to selected exponents.

Adjusted Costs for Carbon Adsorption Unit

1969 costs, not including first charge of carbon

	Kellogg-FWPCA costs,$	Adjustment factor	Adjusted to this estimate,$	% of total
Foundations, etc.	$ 42,000	1.5	63,000	2.4
Carbon adsorbers	670,750	2.2	1,476,000	55.7
Tanks, carbon transport, carbon storage	103,880	1.5	155,800	5.9
Structural steel	20,900	1.5	31,400	1.2
Pumps compressors	65,070	1.2	78,100	2.9
Office buildings	5,400	1.0	5,400	0.2
Regeneration system	128,240	1.5	192,400	7.2
Valves, piping	268,990	1.5	403,500	15.2
Electrical, instrumentation	188,260	1.2	225,900	8.5
Paint, utilities	9,660	1.3	12,600	0.5
Conveying equipment	9,360	1.5	14,000	0.5
	$1,512,510	1.76	$2,658,100	(100.2)

Adjust total cost above to Jan., 1973 by ENR Equipment Index (1812/1216)
= $3,961,000

Cost of First Charge of Carbon

First Charge = 264,000 lb/column x 12 columns = 3,170,000 lb

Warehouse carbon for 30 days of requirements = 1200 lb/day total losses x 30 days = 36,000 lb.

Total inventory of carbon = 3,206,000 lb
Cost at $0.27/lb = 0.27 x 3,206,000 = $865,600
Cost at $0.10/lb = 0.10 x 3,206,000 = $321,000

CAPITAL COST OF pH ADJUSTMENT AFTER LIME TREATMENT

Amount of CO_2 needed to decrease pH from 11.5 to 8.0, as determined from acid titrations of samples from pilot plant runs = 0.018 eq/l or 3.3 lb CO_2/kgal.
Kiln gas needed at 8.4 ft^3/lb and 25 volume-% CO_2 in kiln gas = 3.3 x 8.4/0.25 = 111 ft^3 kiln gas per kgal.
Kiln gas needed per day = 111 x 9,600 = 1,080,000 ft^3 (STP)/day.
Kiln gas at 90% utilization of CO_2 = 1,080,000/0.9 = 1,200,000 SCFD = 833 SCFM.
Retention time for neutralization - allow 10 minutes on basis of results at other plants.
Volume of pH adjust tank = 10 x 9,600,000/1440 = 67,000 gal = 8,900 ft^3.

Diameter of tank = $\sqrt{8900 \times 4/3.14}$ = 28 ft.
Agitation on basis of carbonators at Continental Can plant = 3 at 40 hp ea.
Cost of pH adjust tank, including agitators, gas piping, installation,etc., (29,30,24) - $169,000.

CAPITAL COST OF BACKWASH CLARIFICATION AND SURGE TANKS

Need two 80,000-gal tanks with stirrers and conical bottoms to clarify the washwater after each column is backwashed.
Cost including sludge pumps, installation, etc. = $70,000

OPERATING COSTS FOR LIME TREATMENT

Operating costs for recalcining lime sludge are included in the cost of recalcined lime.
Make-up lime at mill purchase price = 4.7 tons/day x $24.23/ton = $114/day
Calcination of lime in lime sludge at mill operating cost = 16.1 tons/day x $12.40/ton=$200/day
Total cost of lime = $114 + 200 = $314/day, or $319/9600 kgal = $0.0328/kgal

Labor - use 3 man-hours per shift at \$5.85/hr, including fringe benefits=
3 x 3 shifts x \$5.85/9600 kgal = \$0.0055/kgal
Electricity - average costs for lime treatment (5,35) = \$0.0080/kgal

OPERATING COSTS FOR CARBON TREATMENT

Labor - (maintenance labor is included in repair and maintenance factor based on total plant investment)
use 1 operator per shift and 1 lab tachnician per day = 4 man-shifts/day
x 8 hr = 32 x \$5.85/9600 kgal = \$0.0195/kgal
Fuel at 5,700 Btu/lb carbon regenerated (19) and gas at \$0.60/mil Btu =
5,600 x 10^{-6} x \$0.60 = \$0.0034/lb carbon or 2.5 lb/kgal x \$0.0034=
\$0.0085/kgal
Steam - Kellogg report used 1 lb steam/lb carbon regenerated.
cost @ \$0.80/1000 lb = 2.5 lb/kgal x \$0.80/1000 = \$0.0020/kgal
Electricity - experience at large plants for treating municipal effluent
averages \$0.012/kgal. Use this.

TOTAL CAPITAL AND OPERATING COSTS FOR ESTIMATE NO. 1

	Costs	
	At carbon cost of $0.27/lb.	At carbon cost of $0.10/lb.
Capital Costs, $ Million		
Lime treatment	1.680	1.680
Carbon adsorption	3.961	3.961
Backwash tank	0.070	0.070
pH adjust tanks	0.169	0.169
Carbon inventory	0.866	0.321
Total cost of investment, TCI	6.746	6.201
Operating Costs, $/kgal		
Amortization @ 0.0625 TCI/yr	0.1202	0.1105
Repairs and maint. @0.03 TCI/yr	0.0577	0.0530
Taxes and insurance @ 0.02 TCI/yr	0.0387	0.0355
Labor	0.0255	0.0255
Plant overhead at 75% of labor	0.0191	0.0191
Steam	0.0020	0.0020
Gas	0.0085	0.0085
Electricity	0.0200	0.0200
Lime	0.0328	0.0328
Carbon make-up	0.0338	0.0125
Total operating costs, $/kgal	0.3583	0.3194
Operating costs/ton pulp (@ 12 kgal/ton)	$4.30	$3.83

APPENDIX K

ENGLISH TO METRIC UNITS CONVERSION TABLE

English Unit	Abbreviation	Conversion	Abbreviation	Metric Unit
British Thermal Unit	BTU	x 0.2520 =	kg cal	Kilogram - calories
Cubic foot	cu ft	x 0.02832 =	m^3	Cubic meters
Cubic foot	cu ft	x 28.32 =	1	Liters
Degree Fahrenheit	°F	0.555(°F-32) =	C°	Degree Centigrade
Foot	ft	x 0.3048 * =	m	Meters
Gallon (U.S.)	gal	x 3.785 =	1	Liters
Gallons per day per square foot	gpd/sq ft	x 0.04074 =	m^3/m^2 day	Cubic meter per square meter day
Gallons per minute	gpm	x 0.06308 =	1/sec	Liters per second
Gallons per minute per square foot	gpm/sq ft	x 40.7 =	$1/min/m^2$	Liters per minute per square meter
Gallons per ton (of production)	gal/ton	x 4.172 =	1/kkg	Liters per metric ton (1000 kg)
Horsepower	hp	x 0.7457 =	kw	Kilowatts
Inch	in	x 25.4 * =	mm	Millimeters
Million gallons per day	mgd	x 3,785 =	m^3/day	Cubic meters per day
Pound (mass)	lb	x 0.4536 =	kg	Kilograms
Pounds per cubic foot	lb/cu ft	x 16.02 =	kg/m^3	Kilograms per cubic meter
Pounds per square inch	psi	x 703.1 =	kgf/m^2	Kilograms force per square meter
Pounds per thousand gallons	lb/1000 gal	x 119.84 =	g/m^3	Grams per cubic meter
Ton, short	ton	x 0.9072 =	kkg	Metric ton (1000 kilograms)

* Indicates exact conversion factor